Benzene on Graphene: Types of domain boundaries

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It is shown that rich set of linear topological defects - domain boundaries - exist for the system of benzene molecules adsorbed on the graphene surface. This is a typical van der Waals system. Earlier we introduced a vector order parameter (OP) as a transition from symmetric to a stable non-symmetric position and have shown existence of left and right domains connected to a graphene's two-atomic unit cell. Here at the first time we have found existing of the 180°, 120°, 60°, and 0° domain boundaries for relative orientation of OP vectors. We have shown that the domain boundary description requires topology of the neighboring domains (left or right), relative OP vectors direction and length. Additional information can be obtained from the boundary line direction and length. Topological selection rules for possible and forbidden angles of the domain boundaries have been introduced. The number of possible domain pairs (boundaries) and the number of the domain boundaries kinds are calculated. It is noted that the domain and domain boundaries in this system can be artificially created or arise naturally; they can be used for modification of electronic and mechanical properties.

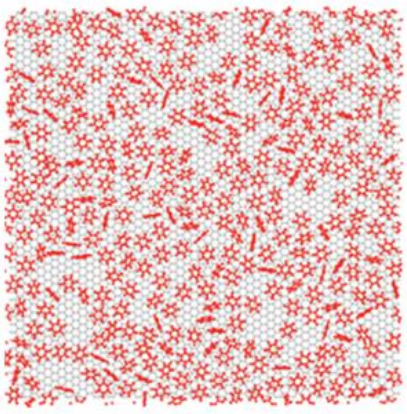


Fig. 1. Snapshot of the first-layer structure relative to the graphene sheet for benzene [1].

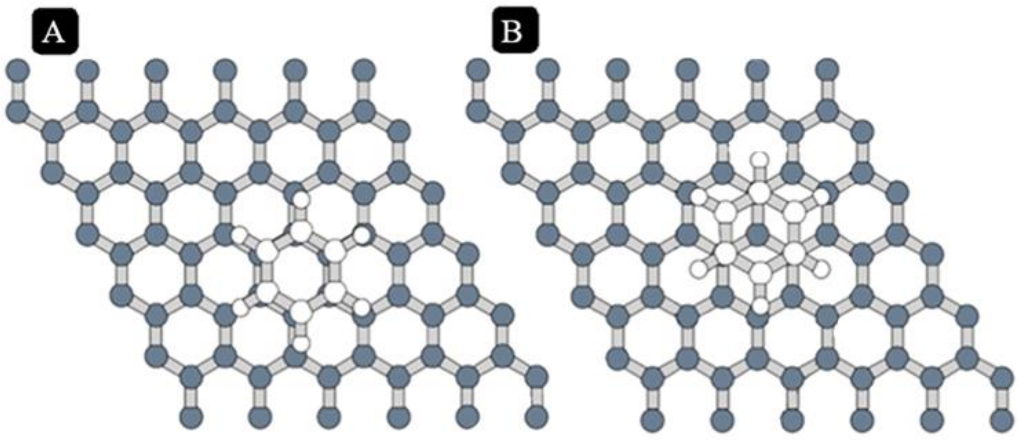


Fig. 2. Schematic view of different adsorption energies, calculated in [2]. The hollow placement (A) has -0.25 eV and the top one (B) has -0.3 eV of adsorption energy.

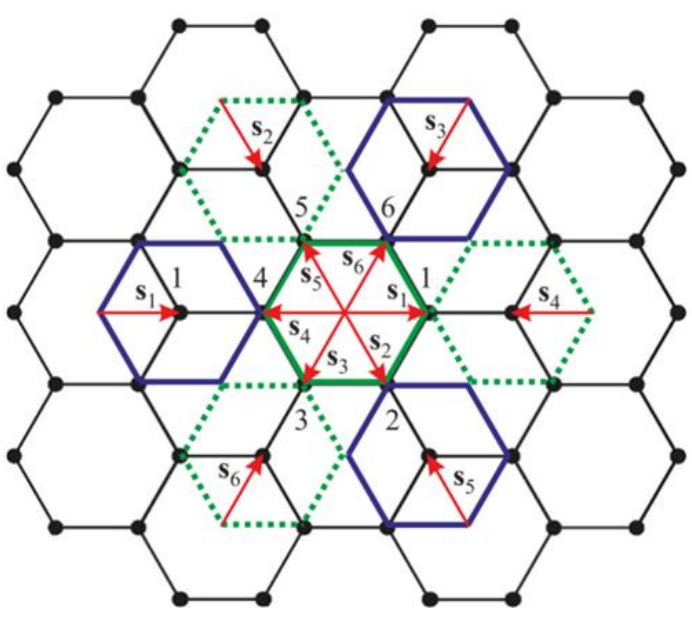


Fig. 3. Schematic view of 6 non-symmetric positions. $\mathbf{s}_i$ (i=1, ..., 6) is an order parameter vector [3].

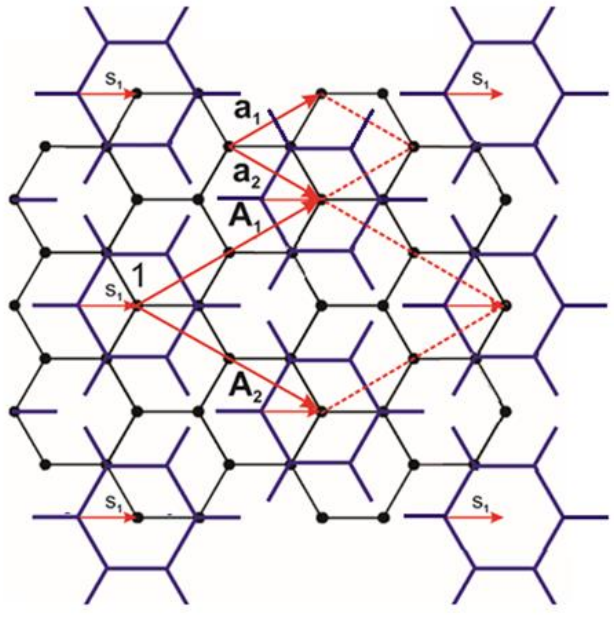


Fig. 4. The vector **a** is a graphene translation and **A** is a benzene translation. The order parameter vector $\mathbf{s}_1$ is shown in this figure [3].

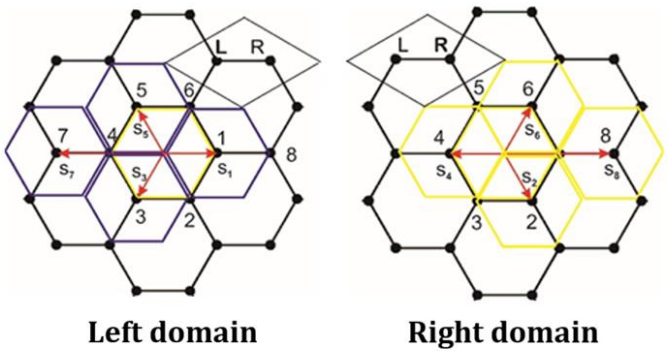


Fig. 5. In this figure, left and right domains are shown; they correspond to left and right bases on the graphene lattice. Domains can be inverted by 180° rotation or mirroring.
Domains corresponding to vectors $\mathbf{s}_1$-$\mathbf{s}_6$ are the main basis domains.
Domains $\mathbf{s}_7$ and $\mathbf{s}_8$ are the additional basis domains. Each vector $\mathbf{s}_7$ or $\mathbf{s}_8$ can have 3 equivalent directions, but only one of them can be realized.

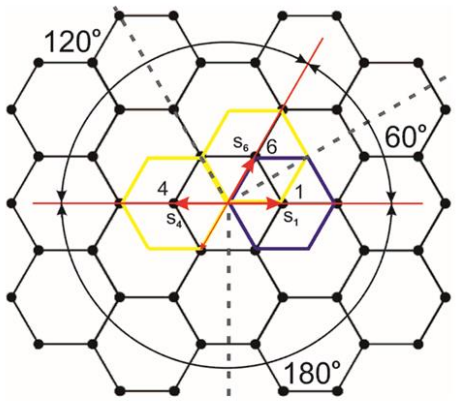


Fig. 6. Domain structure is the consequence of the phase transition theory. The star domain representatives by vectors $\mathbf{s}_1$, $\mathbf{s}_4$, $\mathbf{s}_6$ in the benzene stack structure adsorbed at the graphene surface. The arcs with arrows indicate the angles (60° – $\mathbf{s}_1 \rightarrow \mathbf{s}_6$, 120° – $\mathbf{s}_6 \rightarrow \mathbf{s}_4$, 180° – $\mathbf{s}_1 \rightarrow \mathbf{s}_4$,) between the directions of the star displacements in the domains. The dashed lines indicate possible symmetric directions of the domain walls [3].

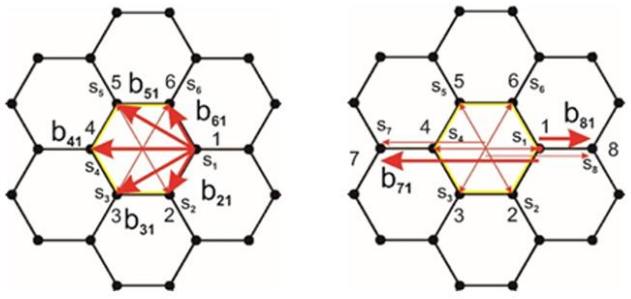


Fig. 7. Left – set of vectors for six main basis transformation vectors ($\mathbf{s}_1$-$\mathbf{s}_6$). Right – additional basis transormation vectors for left and right domains, introduced to fill gaps during translation ($\mathbf{s}_7$, $\mathbf{s}_8$) (see Fig. 5).

$$\mathbf{b}_{k1} = \mathbf{s}_k - \mathbf{s}_1$$

$$k = 2, \ldots, 8.$$

The total number of possible domain boundaries is

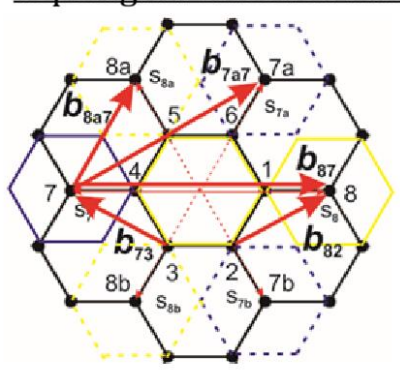
11+10+9+8+7+6+5+4+3+2+1=66.

If we count the main basis domains only, we get

7+6+5+4+3+2+1=28

domain pairs.

Topological selection rules



180° boundaries are possible only between order parameter vectors of equal length that are different in mirror symmetry (left and right) or between order parameter vectors of different lengths that are identical in mirror symmetry (vectors along the points 1-4, 7a-8a and 7b-8b).

120° boundaries are possible only between identical mirror symmetry order parameter vectors of equal length (1-3, 1-5, 7-7b, 8-8a, 7-7a) or between different mirror symmetry order parameter vectors of different lengths (3-8, 2-7, 1-8a, 1-8b).

60° boundaries are possible only between different mirror symmetry order parameter vectors of equal length (7-8a, 7-8b) or the same mirror symmetry order parameter vectors of different lengths (2-8, 3-7).

0° boundaries are possible only between different mirror symmetry order parameter vectors of equal lengths (vectors along the points 1-8, 4-7).

[1]. Oyer, A. J., Carrillo, J. M. Y., Hire, C. C., Schniepp, H. C., Asandei, A. D., Dobrynin, A. V., & Adamson, D. H. (2012). Stabilization of graphene sheets by a structured benzene/hexafluorobenzene mixed solvent. Journal of the American Chemical Society, 134(11), 5018-5021.
[2]. A. Z. Alzahrani, "Structural and electronic properties of graphene upon molecular adsorption: DFT comparative analysis," in Graphene Simulation, ed., J. Cong (InTech Open, Croatia, 2011), p. 376.
[3]. 3. Lykah, V. A., and E. S. Syrkin. "Domains of the adsorbed benzene monolayer on graphene." Low Temperature Physics 48.4 (2022): 353-358.

Conclusions:

1) Initially, the possible molecular position energies of benzene on graphene were studied in terms of DFT. Using the results related to the placement of benzene molecule on graphene, the close-packed domain structure was defined; under the assumption of close packing, all possible domain types were previously found. A vector of order parameter was introduced and a complete basis for defining domains was constructed.
2) The domain boundaries were introduced. It was shown that 180°, 120°, 60°, 0° boundaries exist.
3) The selection rules were introduced for domain boundaries.