Impact of Distributions and Mixtures on the Charge Transfer Properties of Graphene Nanoflakes

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1 Electronic Supplementary Information

In this article we have used the density functional tight-binding method with self-consistent charges (SCC-DFTB), which was implemented in the DFTB+ code,[1] to perform the individual calculations.[2,3] The SCC-DFTB is an approximate quantum chemical approach where the Kohn–Sham density functional is expanded to second order around a reference electron density. The reference density is obtained from self-consistent density functional calculations of weakly confined neutral atoms within the generalised gradient approximation (GGA). The confinement potential is optimised to anticipate the charge density and effective potential in molecules and solids. A minimal valence basis set is used to account explicitly for the two-centre tight-binding matrix elements within the DFT level. The double counting terms in the Coulomb and exchange–correlation potential, as well as the intra-nuclear repulsion are replaced by a universal short-range repulsive potential. All structures have been fully relaxed with a conjugate gradient methodology until forces on each atom were minimized to be less than 10^{-4} a.u. (i.e. $\approx$5 meV/Å). In all the calculations, the "PBC" set of parameters is used to describe the contributions from diatomic interactions of carbon.[4]

This method has been shown to provide good and reliable results for nanographene in the past,[5–7] and data from these studies has been used in the statistical analysis presented in the main text. For convenience, the data from previous works are presented graphically here; reproduced with permission from the original publications.

As pointed out in the main text this study has focussed on using a Boltzmann distribution, but samples grown using different methods and synthesis conditions may be distributed in different ways. Certainly many graphene nanoflakes are produced under kinetically driven conditions, and a variety of different distributions are possible; including the thermodynamic distribution. To give some indication of the impact using different distributions the results for the Boltzmann distribution are compared to a frequency distribution and a Gaussian (normal) distribution in the table below.

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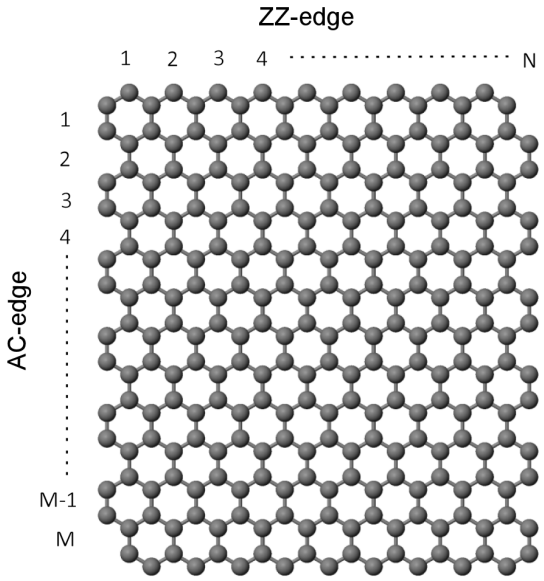

Fig. 1 Matrix for establishing the size and shape of rectangular graphene nanoflakes, as described in reference 7.

Acknowledgments

Computational resources for this project have been supplied by the National Computational Infrastructure national facility under Grant q27.

References

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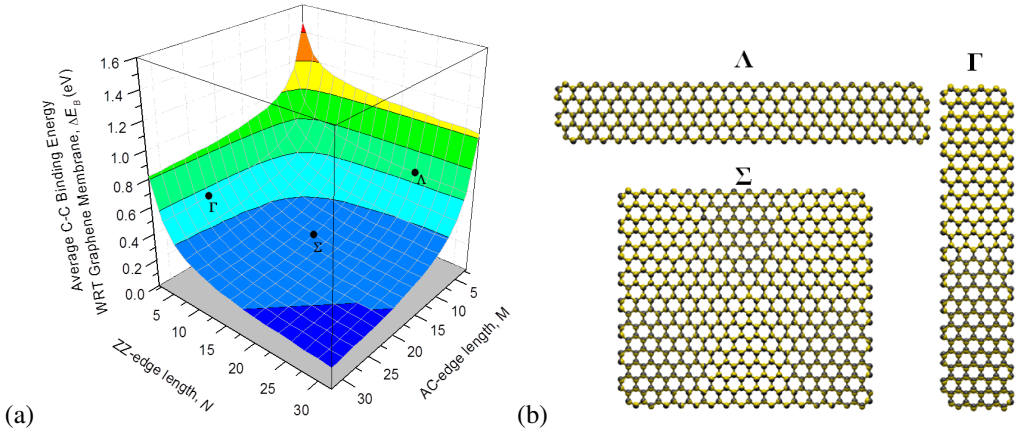
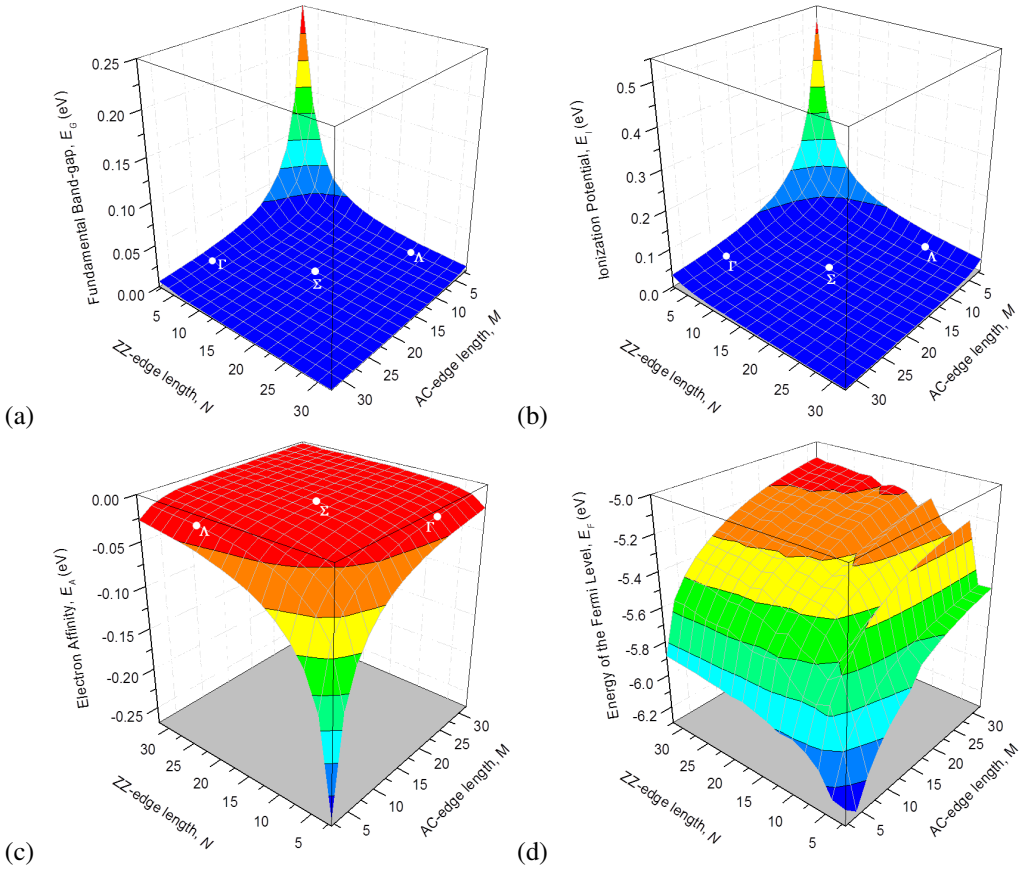


(a) (b)

Fig. 2 (a) Binding energy, (b) sample structure plotted on (a), for the matrix of square and rectangular graphene nanoflakes used in this study, as described in reference 7.



(a) (b) (c) (d)

Fig. 3 Normalised (a) Band gap, (b) ionization potential, (c) electron affinity, and (d) Fermi level for the matrix of square and rectangular graphene nanoflakes used in this study, as described in reference 7.

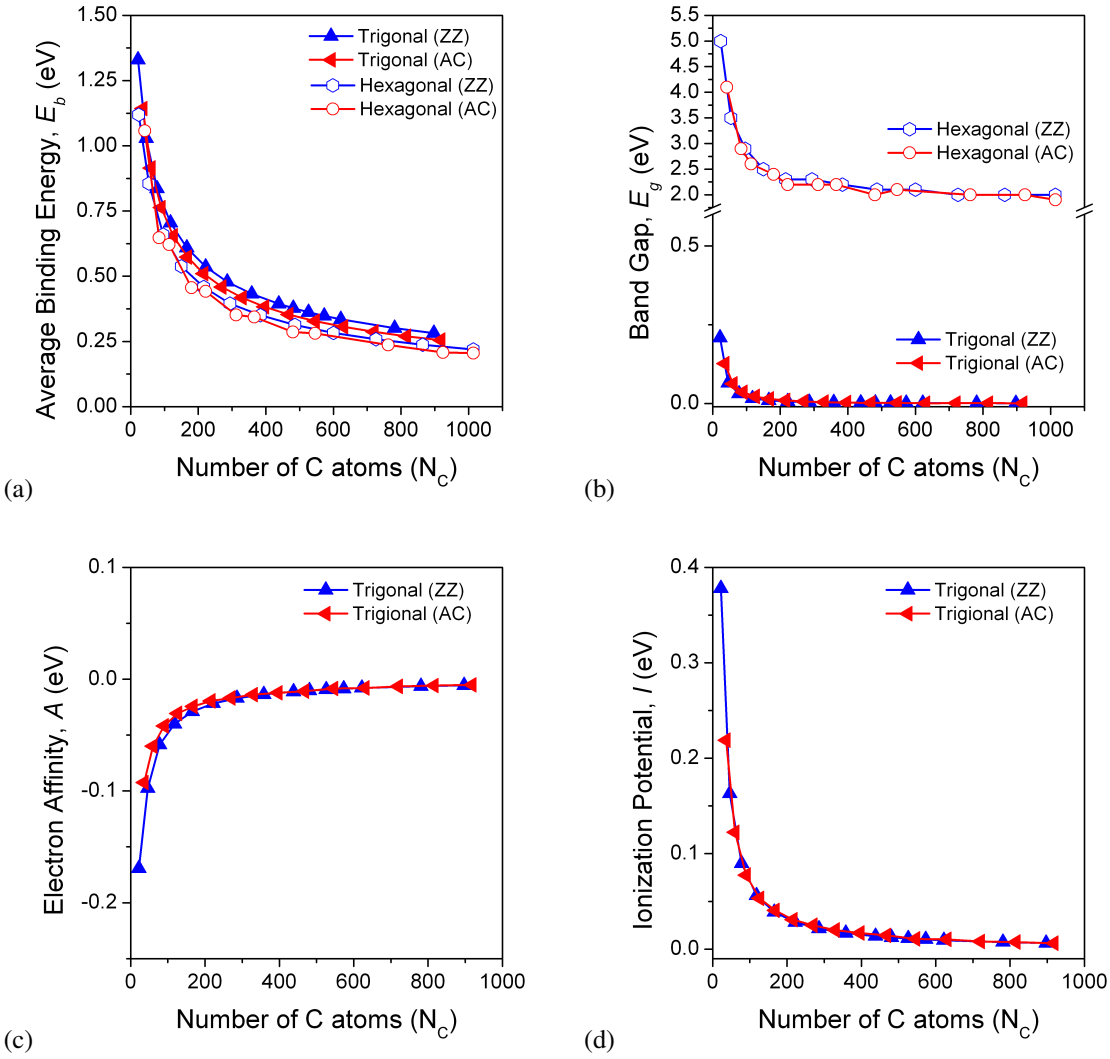


Fig. 4 (a) Binding energy, (b) electronic band gap, (c) electron affinity, and (d) the ionization potential for the hexagonal and trigonal graphene nanoflakes used in this study, as described in references[5] and 6.

Table 1 Comparison of expectation values of properties, and the property resolution (quality factors) for different distributions of graphene nanoflakes. The Gaussian distribution is distributed as a function of the total areas.

Expectation Values	IP (eV)	EA (eV)	E_{gap} (eV)	E_F (eV)	η (eV)	χ (eV)
Boltzman Distribution	5.097	3.891	1.263	-4.504	0.603	4.494
Gaussian Distribution	5.294	4.454	0.851	-4.870	0.420	4.874
Frequency Distribution	5.597	4.299	1.325	-4.949	0.649	4.948
Quality Factors	Q_{IP}	Q_{EA},	$Q_{E_{gap}}$	Q_{E_F}	Q_η	Q_χ
Boltzman Distribution	8.292	6.154	1.302	32.915	1.014	23.916
Gaussian Distribution	8.786	8.460	1.143	12.297	1.056	12.117
Frequency Distribution	7.310	6.224	1.462	9.762	1.266	9.546

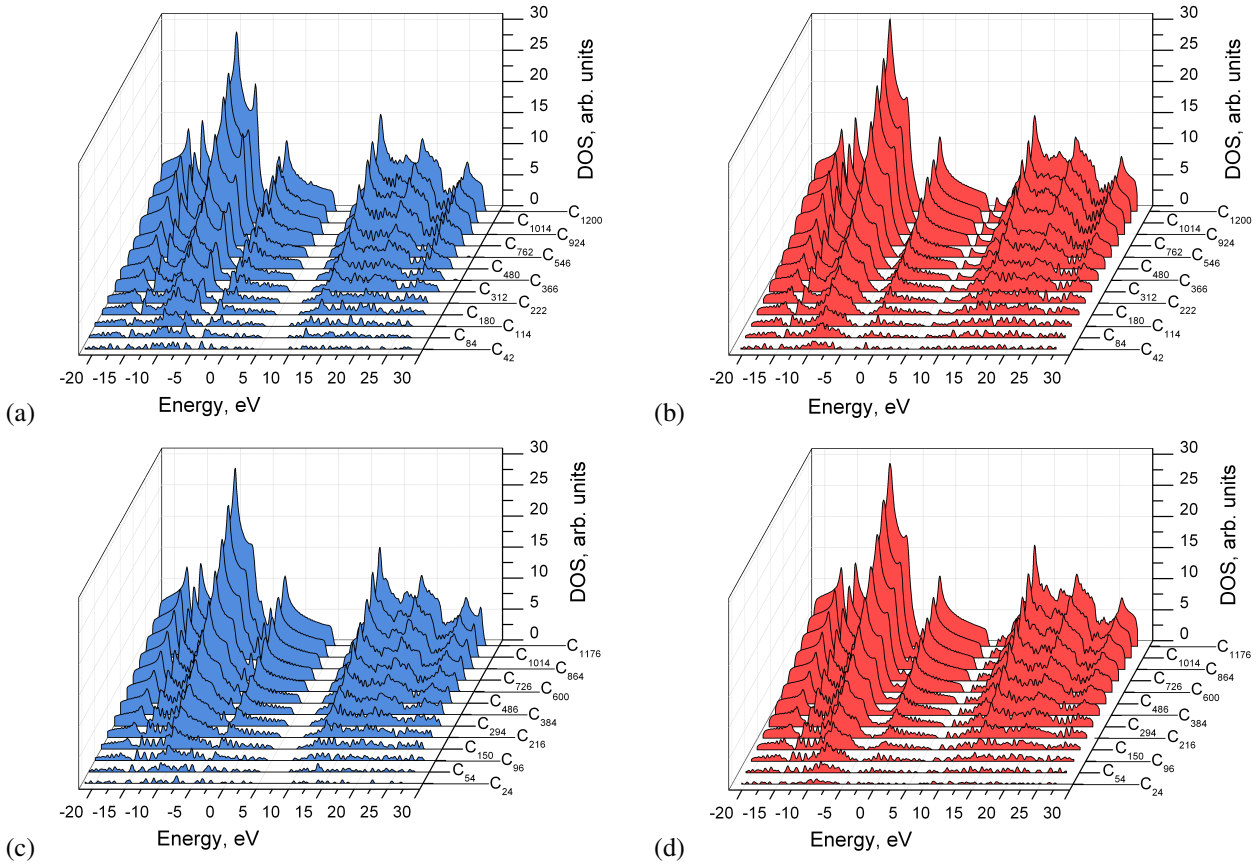


Fig. 5 Density of states for the hexagonal graphene nanoflakes used in this study, as described in reference 5.

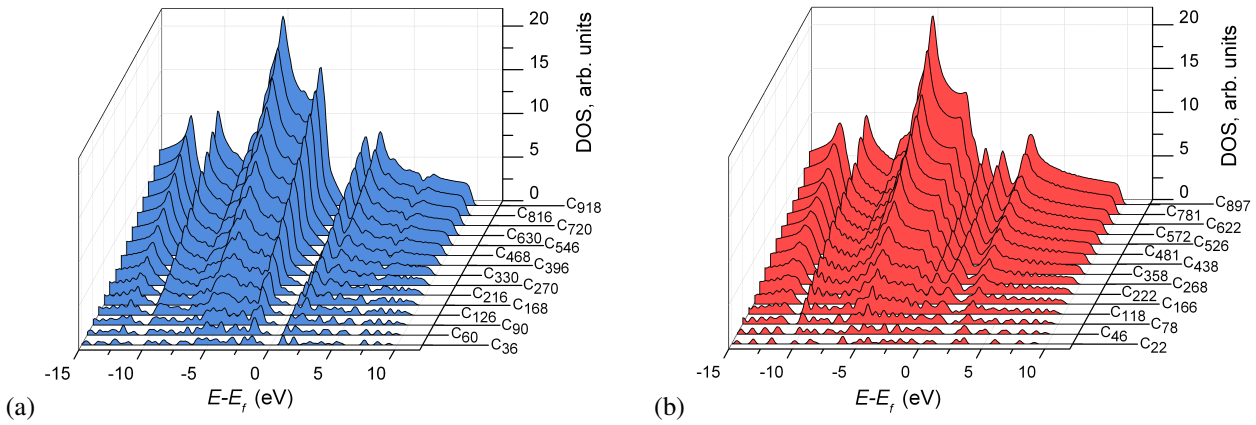


Fig. 6 Density of states for the trigonal graphene nanoflakes used in this study, as described in reference 6.