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Numerical Analysis of Shape Transition in Graphene Nanoribbons

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Abstract

Graphene nanoribbon (GNR) with free edges can exhibit non-flat morphologies due to pre-existing edge stress. Using molecular dynamics (MD) simulations, we investigate the free-edge effect on the shape transition in GNRs with different edge types, including regular (armchair and zigzag), armchair terminated with hydrogen and reconstructed armchair. The results show that initial edge stress and energy are dependent on the edge configurations. It is confirmed that pre-strain on the free edges is a possible way to limit the random shape transition of GNRs. In addition, the influence of surface attachment on the shape transition is also investigated in this work. It is found that surface attachment can lead to periodic ripples in GNRs, dependent on the initial edge configurations.

Key words: Graphene nanoribbon, free edge, shape transition

1. Introduction

Graphene, a monolayer of honeycomb lattice of sp^2 -hybridized carbon atoms, has intriguing properties [1-4]. Recently, increasing research effort has been directed to finite-sized graphene structure, namely graphene nanoribbon (GNR). GNR has demonstrated novel electrical properties such as half-metallic conduction [5] and band-gap opening [6] owing to the existence of free edges. Such free-edge effect can also result in non-zero edge stresses, which may affect the morphology of GNRs, in agreement with experiments [7, 8] and theoretical analysis of thermodynamic stability of 2D membranes [9]. Importantly, there is strong correlation between morphology of GNRs and their electrical properties [10-13]. Consequently, random shape of GNRs caused by structural instability can change the electrical properties and lead to functional failure. Therefore, characterization of

morphologies of GNRs is of essential importance for maintaining their electrical performance. For regular (armchair and zigzag) edges and hydrogen-terminated (r-H) edge in GNRs, compression stress along the length direction was observed [14, 15], resulting in ripples and warping in GNRs [16]. While for reconstructed edges terminated with pentagons-hexagons ring (r-5-6 edge) and pentagons-heptagons ring (r-5-7 edge) [17], they are subject to tension along the length direction, which triggers spontaneous curling of GNRs with tapered ends [18]. In principle, shape transition between all possible morphologies is promoted by external stimuli such as temperature or mechanical loading. Up to date, the free edge effect on shape transition of GNRs has not been well understood.

In the present work, we demonstrate from classical molecular dynamics (MD) simulations that the type of edge termination has critical influence on the shape transition in GNRs. Extensive energetics analysis is conducted to investigate the shape transition in GNRs with regular, hydrogen-terminated and reconstructed edges. The possible ways to control the morphology of GNR is discussed. Given the strong relationship between morphology and functionalities in GNR, our results are useful for the development of GNRs-based devices.

2. Model and methodology

To study shape transition of GNRs and its dependence with edge configurations, atomistic models with regular (armchair and zigzag), r-H and reconstructed edges were built, as shown in Fig. 1. For reconstructed edge, r-5-6 type edge was investigated as previous research showed negligible edge stress in r-5-7 edge configuration [17]. Both periodic boundary conditions (PBCs) and non-PBCs were adopted in the models. For each GNR model, its initial and final configurations were relaxed to a minimum energy state by using conjugate gradient energy minimisation. Then, Nose-Hoover thermostat [19, 20] was employed to equilibrate the system at 0.1 K. In the MD simulations, the adaptive intermolecular reactive bond order (AIREBO) potential [21] implemented in the software package LAMMPS [22]

was used to simulate the formation, separation and rotation of C-C covalent bonds and it can be expressed in terms of

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} E_{kijl}^{TORSION} \right] \quad (1)$$

where E_{ij}^{REBO} is the REBO interaction, based on the form proposed by Tersoff [23]; E_{ij}^{LJ} is the Lennard-Jones (LJ) 12-6 potential; $E_{kijl}^{TORSION}$ is the explicit 4-body potential that describes various dihedral angle preferences in the hydrocarbon systems.

From atomistic-simulation perspective, all possible shapes of GNRs are hardly accessible by direct MD simulations due to time-scale constraint [24, 25]. To overcome this limitation, nudged elastic band (NEB) method [26] was employed to evaluate the minimum energy path (MEP) for shape transition in GNRs, which has been utilized in our previous work [27, 28]. MEP is a continuous path in a $3N_{atom}$ -dimensional configuration space (N_{atom} is the number of free atoms). The atomic forces are zero at any point in the $(3N_{atom}-1)$ -dimensional hyperplane perpendicular to the MEP. The energy barriers for shape transitions can be determined by the saddle points on the MEP. In our calculation, the MEPs in $3N_{atom}$ -dimensional configuration space are determined by 40 equally spaced replicas connected by elastic springs. The calculations converge when the force on each replica is less than 0.03 eV/Å. A continuous MEP is then obtained by polynomial fitting of the discrete MEP [26].

3. Results and discussion

3.1. Shape transition of GNRs with regular and r-H edges

In the cases of regular and r-H free edges, two GNR models with widths of 15.62 Å (width 1) and 71.00 Å (width 2) are used, with both PBCs and non-PBCs along the edge directions. To investigate structural instability of GNRs, we apply the out-of-plane perturbation in the same form as reference [16], i.e.,

$$w(x_1, x_2) = A \sin(kx_1) e^{-x_2/l} \quad (2)$$

where x_1 , x_2 are coordinates in the direction of model length and width, respectively; k is the wave number; A is perturbation amplitude; $l = 0.23\lambda$ is the length scale penetrating into the sheet, and λ is the wave length. Here, we take $k=1\sim 5$ and $A=2.0\text{-}5.0 \text{ \AA}$. By NEB calculations, it can be found that the variation of A has no influence on the final configuration of GNR after energy minimization. Hence only is used in the following analysis. In the MEPs (Fig. 2), the energy barrier E_{eb}^+ for shape transition from State A to State B equals zero. Here, State A represents the initial configuration of GNR and State B represents the final configuration of GNR. This indicates that the initial state of GNR configuration is energetically meta-stable. In other words, it corresponds to a saddle point in the energy landscape (Fig. 2 inset). Subject to even a small perturbation, it falls into a local-minimum energy state nearby and ripples appear in the edge area. From energetic point of view, elongation caused by the perturbation can reduce the pre-existing compressive stress along the free edges and leads to the decrease of total energy, making GNR stay in an thermodynamically (the total energy of final state smaller than that of initial state) [29] and kinetically (zero value of E_{eb}^+) favourable state (State B).

As shown in Fig. 3, the energy barrier E_{eb}^- required to come back to the saddle point, i.e., from State B to State A, is approximately independent on the wave number k of perturbation and GNR width. This may be attributed to the fact that the edge effect is confined within the edge area. The E_{eb}^- for armchair, zigzag and r-H edges is estimated as 0.3 eV, 1.5 eV and 6.0 eV, respectively. This suggests that GNR becomes more energetically stable after hydrogen functionalization. Obviously, when the energy barrier E_{eb}^- is overcome by external thermal or mechanical stimuli, shape transformation among all possible configurations is expected to occur in GNRs.

In order to prevent GNR from transferring into a random corrugated configuration, elastic strain engineering of graphene is expected to play a significant role. Here, small tensile strain was applied to the initial configuration of GNR before introducing the perturbation. We then evaluated the MEPs for shape transition of GNRs at strain $\varepsilon = 1\%$ and $\varepsilon = 3\%$, respectively. Interestingly, the initial strained configuration of GNR is no longer in a meta-stable state. At $\varepsilon = 1\%$ (Fig. 4), the energy barrier E_{eb}^+ becomes non-zero. For regular edge, E_{eb}^+ (about 0.5 eV) is larger than E_{eb}^- (0.3 eV) and therefore the shape transition from State A to State B does not happen. Similarly, as shown in the insert of Fig. 4, the GNR with r-H edge has the minimum initial energy state and tends to maintain a flat configuration. At a higher $\varepsilon = 3\%$ the GNRs with both regular and r-H edges possess the minimum initial energy and therefore are energetically stable (Fig. 5). Therefore, pre-strain in tension is considered to be an effective way to prevent random shape transition in the GNRs with compressive-stressed edges. In addition, a smaller strain is required for the GNRs with hydrogen-termination edge ($\varepsilon = 1\%$). Taking into account the negative thermal expansion coefficient of graphene, tensile strain can be achieved by lowering the temperature [30].

3.2. Shape transition of GNRs with reconstructed edges

As for r-5-6 edges, we only consider GNR models with non-PBCs, to which small out-of-plane perturbation $w(x_1) = A \sin(kx_1)$ is applied. Upon minimization, GNR curls about an axis perpendicular to the edge direction with tapered ends. Different from regular and r-H edges, the initial configuration of GNR with r-5-6 edges is in a local-energy-minimum state (State A) as shown in the inset of Fig. 6. Based on the NEB calculations (Fig. 6), E_{eb}^+ increases with the wave number k as well as amplitude A (not shown in the figure). In addition, E_{eb}^+ for the formation of curling in GNR (Fig. 7) is above 100.0 eV, making such large out-of-plane deformation possible only at extremely high temperatures. Such high E_{eb}^+

is governed by the energetic interplay between C-C potential energy E_{int} and elastic strain energy E_{strain} .

The tensile stress at edges serves as driving force to lower E_{int} against the increase of E_{strain} , so as to minimize the total energy ($E_{\text{int}} + E_{\text{strain}}$). After equilibration, the resulting curling can span the entire size of GNR. Specifically, recent quantum chemical modelling demonstrated that the formation of pentagon rings at edges is one of four critical steps in fullerene formation [31]. Therefore, the study of shape transition for r-5-6 edges provides the fundamental understanding of the formation of some graphene-based nano-structures, such as fullerenes, carbon nanotubes [32] and graphene-coated nanoparticles [33].

3.3. Shape transition of GNRs with surface attachment

During material processing and practical application, the surface of GNRs can interact with other atoms to form surface attachment. However, it is not clear whether or not the surface attachment can play a role in dictating the morphology of GNRs. In this work, the shape transition in GNRs with H atom attachment on the surface is investigated. Both armchair and r-5-6 edges are modelled with non-PBCs. As illustrated in Fig. 8, even two hydrogen atoms can greatly influence the final configurations of GNRs. For the GNR with armchair edge as shown in Fig. 8(a), the C-H bonds can be formed through sp^2 -to- sp^2 bonding transition. Consequently, ripples appear but are confined within the edge areas. For the GNR with r-5-6 edges (Fig. 8(b)), the sp^2 -to- sp^2 bond transition also changes the morphology of GNR. Interestingly, periodic ripples are observed and hydrogen atoms are located on the ridges. In other words, the shape of the GNR is dependent on the locations of H atoms. For GNRs with reconstructed edges, the calculated edge stress in the GNR with H atoms attached on the surface (Fig. 8(b)) is 1.327 eV/\AA , lower than that in GNR without H atom attachment (2.44 eV/\AA). Therefore, H atom attachment can stabilize the GNRs. Even though only hydrogen

atom is studied here, we expect other atoms or functional groups may have similar effect on the morphology of GNR. Surface attachment can provide an alternative approach for controlling the morphology of GNRs or graphene flakes.

4. Conclusions

The free-edge effect on the shape transition of GNRs has been investigated using MD simulations. The analysis results reveal that intrinsic edge stress plays a critical role in the shape transition of GNR. For the regular and r-H edges with compressive edge stresses, initial configuration stays in a meta-state, which will randomly fall into nearby local energy minimum state under a perturbation. Pre-strain in tension can offset the compressive edge stresses and inhibit possible shape transition of GNR. While for the reconstructed (r-5-6) edge with tensile edge stress, initial configuration stays in a local energy minimum (LEM) state. Consequently, external perturbation is required to overcome the energy barrier for transition to other morphologies (e.g. curling). It was found that surface attachment could significantly influence the morphology of GNRs, especially for those with reconstructed edges. These results can shed some light on the way to control the shape transition in GNRs.

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, *Science*. 306 (2004) 666-9.
- [2] Y. Zhang, Y.-W. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature (London)*. 438 (2005) 201-4.
- [3] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science*. 321 (2008) 385-8.
- [4] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Superior Thermal Conductivity of Single-Layer Graphene, *Nano Lett.* 8 (2008) 902-7.

- [5] Y.-W. Son, M.L. Cohen, S.G. Louie, Half-metallic graphene nanoribbons, *Nature (London)*. 444 (2006) 347-9.
- [6] M.Y. Han, B. Özyilmaz, Y. Zhang, P. Kim, Energy Band-Gap Engineering of Graphene Nanoribbons, *Phys Rev Lett*. 98 (2007) 206805.
- [7] J.C. Meyer, A.K. Geim, M.I. Katsnelson, K.S. Novoselov, T.J. Booth, S. Roth, The structure of suspended graphene sheets, *Nature (London)*. 446 (2007) 60-3.
- [8] Z. Li, Z. Cheng, R. Wang, Q. Li, Y. Fang, Spontaneous Formation of Nanostructures in Graphene, *Nano Lett*. 9 (2009) 3599-602.
- [9] D.R. Nelson, L. Peliti, Fluctuations in membranes with crystalline and hexatic order, *J Phys-Paris*. 48 (1987) 1085-92.
- [10] F. Guinea, M.I. Katsnelson, M.A.H. Vozmediano, Midgap states and charge inhomogeneities in corrugated graphene, *Phys Rev B*. 77 (2008) 075422.
- [11] V.M. Pereira, A.H. Castro Neto, Strain Engineering of Graphene's Electronic Structure, *Phys Rev Lett*. 103 (2009) 046801.
- [12] F. Guinea, M.I. Katsnelson, A.K. Geim, Energy gaps and a zero-field quantum Hall effect in graphene by strain engineering, *Nat Phys*. 6 (2010) 30-3.
- [13] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, The electronic properties of graphene, *Rev Mod Phys*. 81 (2009) 109-62.
- [14] S. Jun, Density-functional study of edge stress in graphene, *Phys Rev B*. 78 (2008) 073405.
- [15] B. Huang, M. Liu, N. Su, J. Wu, W. Duan, B.-I. Gu, F. Liu, Quantum Manifestations of Graphene Edge Stress and Edge Instability: A First-Principles Study, *Phys Rev Lett*. 102 (2009) 166404.
- [16] V.B. Shenoy, C.D. Reddy, A. Ramasubramaniam, Y.W. Zhang, Edge-Stress-Induced Warping of Graphene Sheets and Nanoribbons, *Phys Rev Lett*. 101 (2008) 245501.
- [17] C.D. Reddy, A. Ramasubramaniam, V.B. Shenoy, Y.-W. Zhang, Edge elastic properties of defect-free single-layer graphene sheets, *Appl Phys Lett*. 94 (2009) 101904-3.
- [18] V.B. Shenoy, C.D. Reddy, Y.-W. Zhang, Spontaneous Curling of Graphene Sheets with Reconstructed Edges, *ACS Nano*. 4 (2010) 4840-4.

- [19] W.G. Hoover, Canonical dynamics: Equilibrium phase-space distributions, *Phys Rev A*. 31 (1985) 1695.
- [20] S. Nosé, A unified formulation of the constant temperature molecular dynamics methods, *J Chem Phys*. 81 (1984) 511-19.
- [21] S.J. Stuart, A.B. Tutein, J.A. Harrison, A reactive potential for hydrocarbons with intermolecular interactions, *J Chem Phys*. 112 (2000) 6472-86.
- [22] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J Comput Phys*. 117 (1995) 1-19.
- [23] J. Tersoff, Empirical Interatomic Potential for Carbon, with Applications to Amorphous Carbon, *Phys Rev Lett*. 61 (1988) 2879.
- [24] A.F. Voter, F. Montalenti, T.C. Germann, Extending the time scale in atomistic simulation of materials, *Ann Rev Mater Res*. 32 (2002) 321-46.
- [25] A. Kushima, J. Eapen, J. Li, S. Yip, T. Zhu, Time scale bridging in atomistic simulation of slow dynamics: viscous relaxation and defect activation, *Eur Phys J B*. 82 (2011) 271-93.
- [26] G. Henkelman, H. Jónsson, Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points, *J Chem Phys*. 113 (2000) 9978-85.
- [27] M.C. Wang, C. Yan, L. Ma, N. Hu, M.W. Chen, Effect of defects on fracture strength of graphene sheets, *Computational Materials Science*. 54 (2012) 236-9.
- [28] M.C. Wang, C. Yan, L. Ma, N. Hu, Molecular dynamics investigation on edge stress and shape transition in graphene nanoribbons, *Computational Materials Science*. 68 (2013) 138-41.
- [29] S. Huang, S. Zhang, T. Belytschko, S.S. Terdalkar, T. Zhu, Mechanics of nanocrack: Fracture, dislocation emission, and amorphization, *J Mech Phys Solids*. 57 (2009) 840-50.
- [30] W. Bao, F. Miao, Z. Chen, H. Zhang, W. Jang, C. Dames, C.N. Lau, Controlled ripple texturing of suspended graphene and ultrathin graphite membranes, *Nat Nanotechnol*. 4 (2009) 562-6.
- [31] A. Chuvilin, U. Kaiser, E. Bichoutskaia, N.A. Besley, A.N. Khlobystov, Direct transformation of graphene to fullerene, *Nat Chem*. 2 (2010) 450-3.
- [32] E.L. Yurii, M.P. Andrei, Formation and growth of carbon nanostructures: fullerenes, nanoparticles, nanotubes and cones, *Phys-Usp+*. 40 (1997) 717.

[33] N.A. Luechinger, N. Booth, G. Heness, S. Bandyopadhyay, R.N. Grass, W.J. Stark, Surfactant-free, melt-processable metal-polymer hybrid materials: Use of graphene as a dispersing agent, *Adv Mater.* 20 (2008) 3044-9.

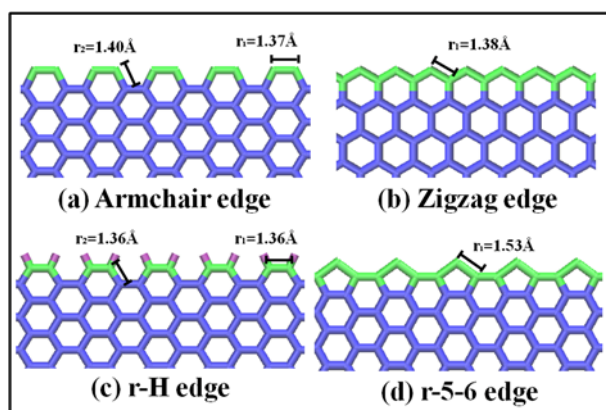


Figure 1 – Atomistic structures of GNRs with four different types of free edges: (a) armchair edge, (b) zigzag edge, (c) hydrogen-terminated (r-H) edge and (d) pentagons-hexagons ring (r-5-6) edge.

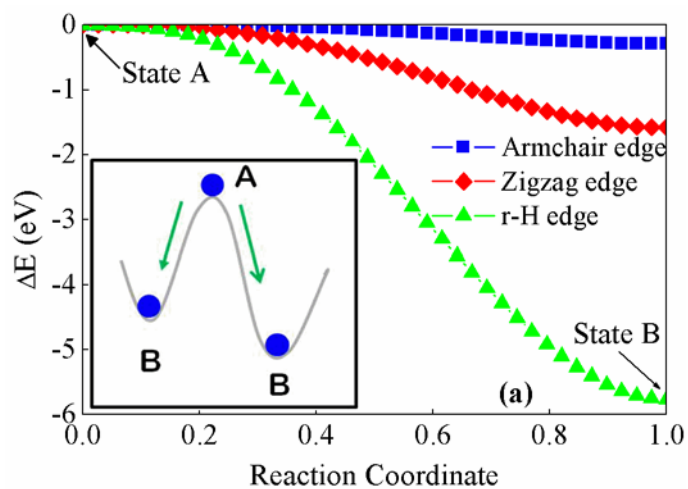


Figure 2 – The minimum energy paths (MEPs) for shape transition of GNRs with armchair edge (red color), zigzag edge (red color) and r-H edge (green color). The inset shows the schematic description of energy landscape for shape transition.

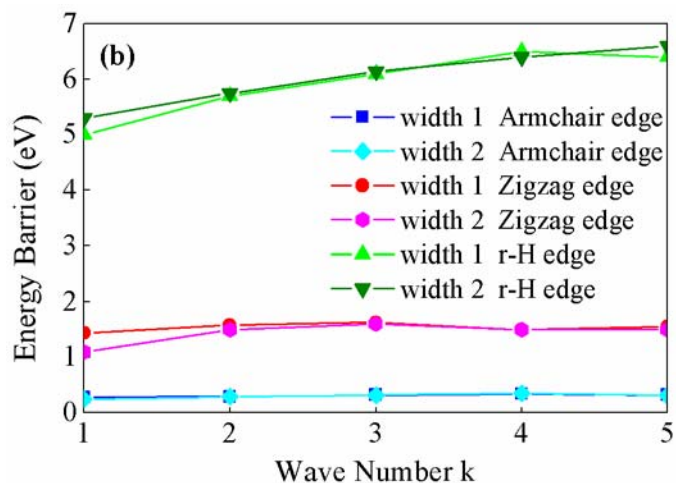


Figure 3 – The energy barrier E_{eb}^+ for shape transition of GNRs with different free edges (armchair, zigzag and r-H) and widths with respect to the wave number k of out-of-plane perturbation.

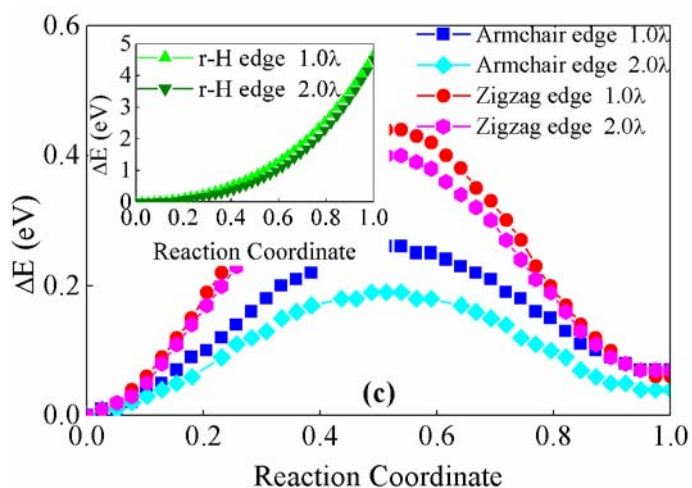


Figure 4 - The minimum energy paths (MEPs) for shape transition of GNRs with different free edges (armchair, zigzag and r-H) and the wave number of out-of-plane perturbation ($k=1.0, 2.0$) at strain $\varepsilon = 1\%$.

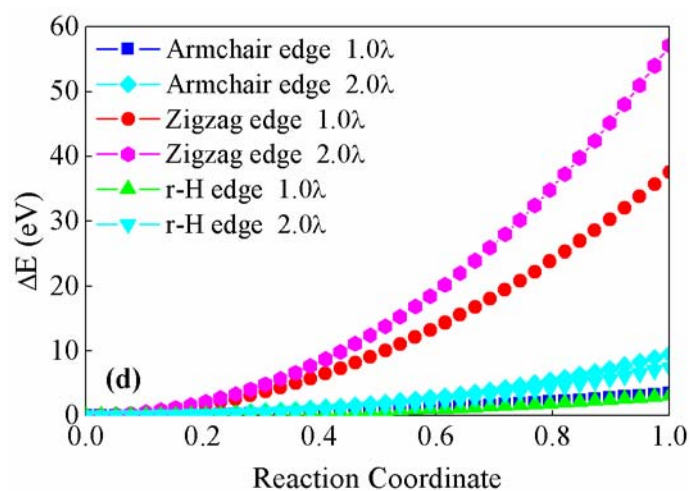


Figure 5 - The minimum energy paths (MEPs) for shape transition of GNRs with different free edges (armchair, zigzag and r-H) and the wave number of out-of-plane perturbation ($k=1.0, 2.0$) at strain $\varepsilon = 3\%$.

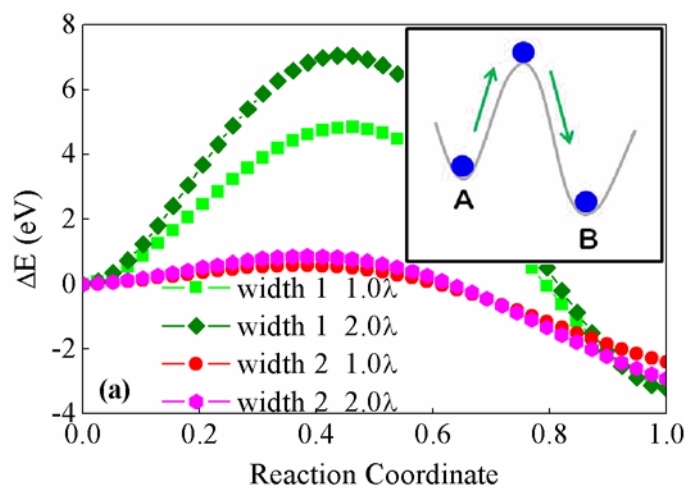


Figure 6 – The minimum energy paths (MEPs) for shape transition of GNRs with r-5-6 edge, different widths and wave number of out-of-plane perturbation. The inset shows the schematic description of energy landscape for shape transition.

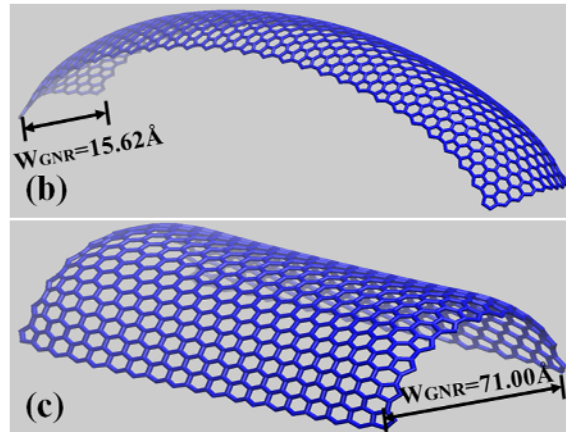


Figure 7 – Atomistic morphology of GNRs with r-5-6 edges and different widths (a) 15.62 Å, (b) 71.00Å.

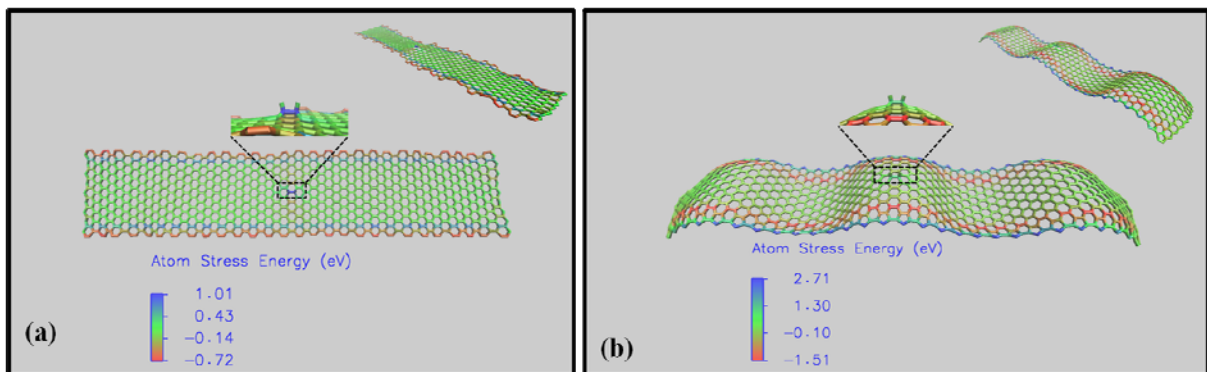


Figure 8 - Distribution of atom stress energy in GNRs with (a) armchair edge and (b) r-5-6 edge. Insets show the corresponding morphologies of both cases, respectively.