Effect of vacancy distribution on the relaxation properties of graphene: a molecular dynamics study

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Influence of vacancies on the relaxation properties of graphene nanoribbons has been investigated by molecular dynamics simulation in several nanometre sizes. Moreover, three factors including vacancy size, number and distribution are taken into consideration. The results show graphene nanoribbons present different kinds of deformation at different sites with various vacancy distributions. The effects of vacancy distributions on the relaxation properties of graphene nanoribbons are discussed.

1. Introduction: Graphene, also called two-dimensional graphite, is a new type of low-dimensional material following the discovery of fullerenes and carbon nanotubes. In recent years, graphene has attracted considerable interest because of its extraordinary electrical, thermal and mechanical properties arising from its unique structure [1, 2]. However, a variety of defects including topological defects [3, 4], vacancy [5–10] and adatom [11–14] are inevitably produced into graphene during the preparation process. Ideally, researchers would like to determine the physical properties of a single-layer graphene sheet by experimental technology. However, graphene sheet must be attached to the substrate, which affects the properties of graphene. Molecular dynamics (MD) simulation enables us to follow and understand the structure and dynamics with extreme detail where motion of individual atoms can be tracked [15, 16]. The relaxation properties of graphene have been a hot subject in many investigations because the graphene sheets have undergone significant distortion from the defects and vacancies, which could influence its electronic and mechanical properties. The relaxation is essential for understanding the morphological evolution, dispersibility and interface compatibility in composites. Recently, MD simulation has been a useful tool to study the relaxation properties of graphene [17–19]. In this Letter, MD method has been employed to simulate the evolution of dynamic equilibrium of graphene with vacancies in the relaxation process. The effect of defect type, number and location on the relaxation properties of graphene was discussed.

2. Physical models and simulation methods: Position and size of vacancies in graphene ribbons are shown in Fig. 1. Graphene is a crystalline structure composed entirely of carbon atoms with a honeycomb-like pattern. The length of the C–C bond is ~0.142 nm and the thickness is 0.335 nm. A typical vacancy is created by removing carbon atoms at the corners of a hexagon and subsequently by terminating the remaining six two-fold coordinated carbon atoms with hydrogen atoms.

As shown in Fig. 2, the dimension of the simulation model was around 79.54 Å × 46.80 Å. Three types of configurations and seven different distributions of vacancies are named as follows: *T–D–N*, where *T* means the type of vacancies, including 1, 2 and 3; *D* means the distribution of vacancies, including the bottom of the *x*-direction (BX), the side of the *y*-direction (LY), the middle of the *x*-direction (MX), the middle of the *y*-direction (MY) and a wide distribution (*W*); and *N* means the number of the vacancies. The relaxation properties of the perfect graphene and the graphene with the vacancies were simulated.

Large-scale atomic/molecular massively parallel simulator (LAMMPS) is a versatile and open source code for performing MD simulations of coarse-grained models. The adaptive inter-molecular reactive empirical bond order potential (AIREBO),

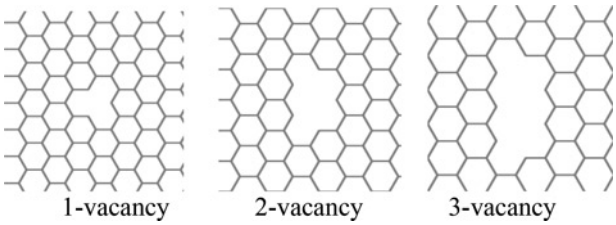

Fig. 1 *Position and size of vacancies in graphene ribbons*

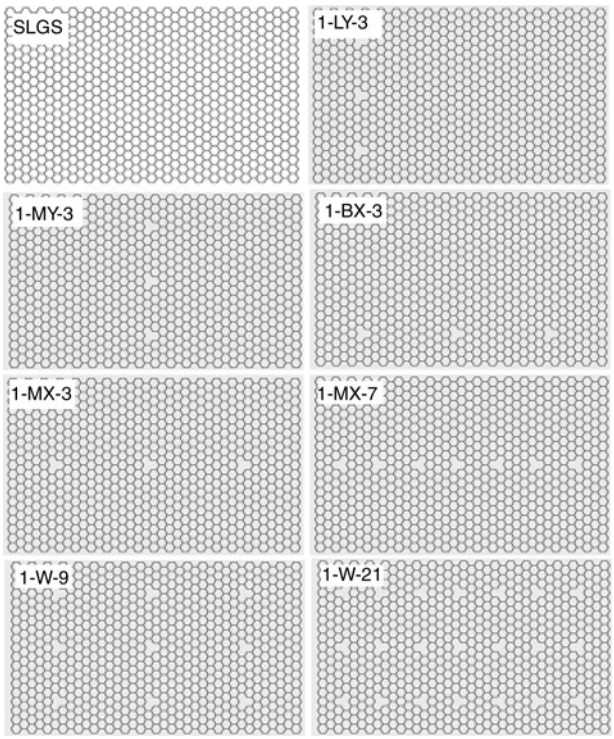

Fig. 2 *Schematic showing the positions and the numbers of vacancies*

included in the LAMMPS software package was employed to model the inter-atomic forces present in the covalent binding of carbon in the graphene. AIREBO potential consists of three terms

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

Periodic boundary condition is imposed on the x- and y-directions without applying any external constraints and loads. The length of C–C bonds is set at 1.30–1.54 Å with a cut-off parameter of 1.7 Å. The temperature is controlled at 0.01 K and the simulation time step is 1 fs.

3. Results and analysis: Atomic configurations of graphene after complete relaxation are shown in Fig. 3. The common undulating surface morphology is observed at the edge of the model after complete relaxation. Our data agree with other simulation results with different boundary conditions and temperature [20]. The largest normal displacement depends on the type, location and the number of the vacancies. With widely distributed and large size vacancies (such as 3W9, 3A21), the ripples not only occur at the edges, but also on the internal of graphene, which is similar to the results observed by transmission electron microscopy [21, 22]. This phenomenon could be attributed to the decrease of the constraint force of carbon atoms around the C–C bonds.

To analyse the models more accurately, we track the atom that occurs at the position of maximum displacement. Absolute displacement of the tracking atom in the normal direction was shown in Fig. 4. With the vacancies on the short edge (LY), model 1-LY-3 has the maximum displacement of 6 Å (Fig. 4*a*). The displacement decreases when the vacancies move to the middle of the y-direction (Fig. 4*b*). When the vacancies occur at the bottom of the x-direction, the maximum normal displacements of model 1-BX-3 and 2-BX-3 are approximately the same value (Fig. 4*c*). With the increase of size and number in the middle of the x-direction, same trend is obtained (Figs. 4*d* and *e*). The maximum displacement reaches ~6 Å with the vacancy number of 9, and then it increases to ~9 Å with the vacancy number of 21 (Figs. 4*f* and *g*). For all the three types of the vacancies, the displacements of model 1-W-9, 1-W-21, 1-LY-3, 2-W-9, 2-BX-3, 3-W-21 and 3-CX-7 are all larger than 5 Å (Figs. 4*i* and *j*). It was found that the morphology, location and size of the maximum displacement are affected by the types, positions and

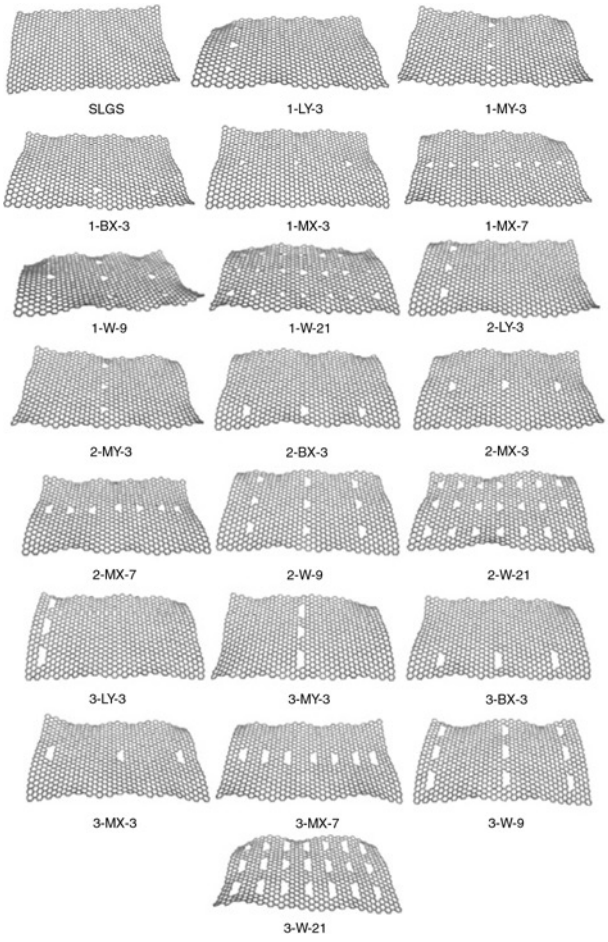

Fig. 3 *Atomic configuration of graphene after relaxation*

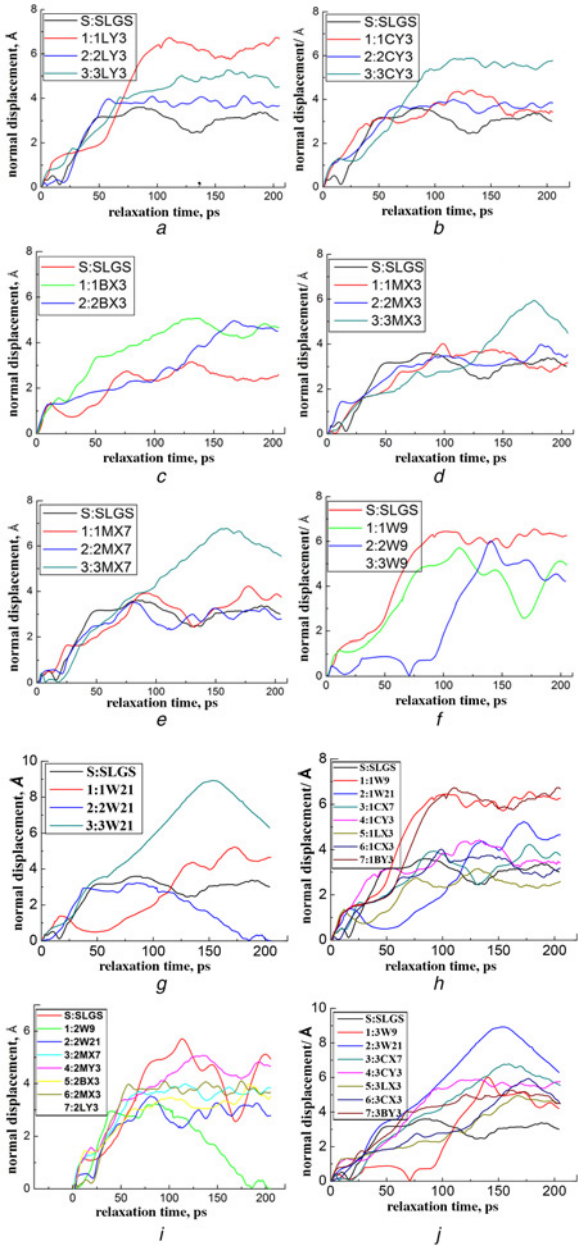

Fig. 4 *Absolute displacement in the normal direction at different relaxation time. Model 1-LY-3, 2-LY-3 and 3-LY-3(a); Model 2-CY-3, 2-CY-3 and 3-CY-3(b); Model 1-BY-3 and 2-BY-3(c); Model 1-MY-3, 2-MY-3 and 3-MY-3(d); Model 1-MX-7, 2-MX-7 and 3-MX-7(e); Model 1-W-9, 2-W-9 and 3-W-9(f); Model 1-W-21, 2-W-21 and 3-W-21(g); Models with first type of vacancy (h); Models with second type of vacancy (i); Models with third type of vacancy (j)*

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the number of the vacancies in the graphene. For lower distribution density, the normal displacement becomes smaller. Introduction of the vacancies should increase the energy of the system. The bond-length variation cannot remove the effects and out-of-plane displacement occurs.

4. Conclusion: The relaxation properties of graphene nanoribbons with different types of vacancies have been studied by MD simulation. In a natural state, graphene is not perfectly flat with corrugated wrinkles appearing at the edge, but not obvious in the inner of graphene. In the case of large size vacancies, the ripples can be observed both at the edge and inner of graphene. The maximum normal displacement increases with the increase of size and the number of the vacancies.

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6 References

[1] Geim A.K., Novoselov K.S.: 'The rise of graphene', *Nat. Mater.*, 2007, **6**, (3), pp. 183–191
[2] Novoselov K.S., Geim A.K., Morozov S.V., *ET AL.*: 'Electric field effect in atomically thin carbon films', *Science*, 2004, **306**, (5696), pp. 666–669
[3] Stone A.J., Wales D.J.: 'Theoretical studies of icosahedral C60 and some related species', *Chem. Phys. Lett.*, 1986, **128**, (5), pp. 501–503
[4] Xu S.C., Irle S., Musaev D.G., *ET AL.*: 'Quantum chemical study of the dissociative adsorption of OH and H_2O on pristine and defective graphite (0001) surfaces: reaction mechanisms and kinetics', *J. Phys. Chem. C*, 2007, **111**, (3), pp. 1355–1365
[5] Telling R.H., Ewels C.P., Ahlam A., *ET AL.*: 'Wigner defects bridge the graphite gap', *Nat. Mater.*, 2003, **2**, (5), pp. 333–337
[6] El-Barbary A.A., Telling R.H., Ewels C.P., *ET AL.*: 'Structure and energetics of the vacancy in graphite', *Phys. Rev. B*, 2003, **68**, (14), p. 144107
[7] Krasheninnikov A.V., Nordlund K., Lehtinen P.O., *ET AL.*: 'Adsorption and migration of carbon adatoms on carbon nanotubes: density-functional ab initio and tight-binding studies', *Phys. Rev. B*, 2004, **69**, (7), p. 073402
[8] Krasheninnikov A.V., Nordlund K., Sirvio M., *ET AL.*: 'Formation of ion-irradiation-induced atomic-scale defects on walls of carbon nanotubes', *Phys. Rev. B*, 2001, **63**, (24), p. 245405
[9] Amorim R.G., Fazzio A., Antonelli A., *ET AL.*: 'Divacancies in graphene and carbon nanotubes', *Nano Lett.*, 2007, **7**, (8), pp. 2459–2462
[10] Lee G.-D., Wang C.Z., Yoon E., *ET AL.*: 'Diffusion, coalescence, and reconstruction of vacancy defects in graphene layers', *Phys. Rev. Lett.*, 2005, **95**, (20), p. 205501
[11] Lehtinen P.O., Foster A.S., Ayuela A., *ET AL.*: 'Magnetic properties and diffusion of adatoms on a graphene sheet', *Phys. Rev. Lett.*, 2003, **91**, (1), p. 017202
[12] Nordlund K., Keinonen J., Mattila T.: 'Formation of ion irradiation induced small-scale defects on graphite surfaces', *Phys. Rev. Lett.*, 1996, **77**, (4), pp. 699–702
[13] Talapatra S., Ganesan P.G., Kim T., *ET AL.*: 'Irradiation-induced magnetism in carbon nanostructures', *Phys. Rev. Lett.*, 2005, **95**, (9), p. 097201
[14] Ma Y., Foster A.S., Krasheninnikov A.V., *ET AL.*: 'Nitrogen in graphite and carbon nanotubes: magnetism and mobility', *Phys. Rev. B*, 2005, **72**, (20), p. 205416
[15] Tapia A., Peon-Escalante R., Villanueva C., *ET AL.*: 'Influence of vacancies on the elastic properties of a graphene sheet', *Comput. Mater. Sci.*, 2012, **55**, pp. 255–262
[16] Wang M.C., Yan C., Ma L., *ET AL.*: 'Effect of defects on fracture strength of graphene sheets', *Comput. Mater. Sci.*, 2012, **54**, pp. 236–239
[17] Zhao H., Min K., Aluru N.R.: 'Size and chirality dependent elastic properties of graphene nanoribbons under uniaxial tension', *Nano Lett.*, 2009, **9**, (8), pp. 3012–3015
[18] Han T., He P.: 'Molecular dynamics simulation of relaxation properties of graphene sheets', *Acta Phys. Sin.*, 2010, **5**, (59), pp. 3408–3413
[19] Wang W.-D., Hao Y., Ji X., *ET AL.*: 'Relaxation properties of graphene nanoribbons at different ambient temperatures: a molecular dynamics study', *Acta Phys. Sin.*, 2012, **20**, (61), pp. 53–63
[20] Ishigami M., Chen J.H., Cullen W.G., *ET AL.*: 'Atomic structure of graphene on SiO2', *Nano Lett.*, 2007, **7**, (6), pp. 1643–1648
[21] Meyer J.C., Geim A.K., Katsnelson M.I., *ET AL.*: 'The structure of suspended graphene sheets', *Nature*, 2007, **446**, (7131), pp. 60–63
[22] Meyer J.C., Geim A.K., Katsnelson M.I., *ET AL.*: 'On the roughness of single-and bi-layer graphene membranes', *Solid State Commun.*, 2007, **143**, (1), pp. 101–109