Graphene-based Nanoscale version of da Vinci’s Reciprocal Structures

Alexandre F. Fonseca and Douglas S. Galvão

Applied Physics Department, Institute of Physics “Gleb Wataghin”, State University of Campinas, Campinas, SP, 13083-970, Brazil.

A reciprocal structure (RS) is a mechanical resistant structure formed by a set of self-supporting elements satisfying certain conditions of structural reciprocity (SR)\(^1\). The first condition is that each element of the structure has to support and be supported by the others. The second condition is that these functions cannot occur in the same part of the element. These two properties make beams and two-dimensional materials very much appropriate to build RSs. Commonly seen in floors or roofs, SR is also present in art, religious symbols and decorative objects. Da Vinci\(^2\) has drawn several examples of such RSs. Here, we propose a simple nano version of a da Vinci’s RS based on graphene nanoribbons. The stability and resistance against mechanical impacts (ballistic projectile) were investigated through fully atomistic molecular dynamics (MD) simulations. We considered structures with three and four joins with and without RS topologies. Our MD results showed that structures with RS topologies are more impact resistant than those without SR, despite the fact that the used graphene nanoribbons are highly pliable. We discuss these results in terms of number of joins, energy absorption and stress on the structures. We discuss possible applications in nanoengineering.

Structural reciprocity (SR) is a concept of self-supporting of load-bearing bars that together form larger mechanical resistant structures\(^1\). Dating back to the Neolithic, SR was found from native tepees and tents, to old bridges like the one over the Rhine that was built in the Roman Empire by Julius Caesar. The drawings of Leonardo da Vinci\(^2\) show structures satisfying SR. Commonly seen in floors or roofs, SR is also present in art, religious symbols and decorative objects. Although SR involves a mutual exchange of action and reaction between parts of the whole structure, it is also known to rely on a perfect symmetric relationship between them\(^1\). A
structure having SR is called reciprocal structure (RS). The main characteristics of a RS are, first, the role of supporting and being supported should not occur in the same part of the structure, i.e., they must be separated, not overlapping like in truss bars. Second, each element of a RS must, at the same time, support the others and being supported by the others. These two properties make beams and two-dimensional materials very much appropriate to build RSs. Figure 1 shows two examples of da Vinci’s RSs with three and four folds. These structures are also called reciprocal frames and it is a matter of architectural applications worldwide.

Here, we present a study of some simple nano versions of two da Vinci’s RSs based on graphene nanoribbons (structures shown at the right side of Figure 1). Thermal stability and mechanical resistance against impacts (from ballistic projectiles) were investigated through fully atomistic molecular dynamics (MD) simulations. We used the AIREBO potential as available in the LAMMPS computational package. We considered two different structures with three and four joins, with and without RS topologies, for comparison. Our MD results showed that structures with RS topologies of four-fold are more impact resistant than that without structural reciprocity, despite the fact that the used graphene nanoribbons are highly pliable. We also analyzed the local structures after equilibration at room temperature. We discuss these results in terms of the flexure of graphene and possible applications in building self-sustained and resistant nano-domes and nanocages, as well as possible applications in nanoengineering.

In order to address the issue of mechanical resistance, we generated not only the 3- and 4-fold graphene-based RSs (right side of Figure 1) but also 3- and 4-fold graphene-based non-RSs as shown in Figure 2. The non-RSs were built by placing one or more graphene nanoribbons on top or bottom of the other nanoribbons, so breaking the rule of RSs of having each element of the structure supporting and being supported by the others. All graphene nanoribbons were Hydrogen passivated to avoid the formation of chemical bonds. The nanoribbons interact only via van der Waals interactions.
Figure 1: Two examples of da Vinci’s RSs studied here, with three (top row) and four (bottom row) folds. On the left, the RS models, and on the right the graphene nanoribbons-based RSs.

Figure 2: Graphene-based RSs (left column) and corresponding non-RSs (right column). In the non-RSs, one or more graphene nanoribbons are placed on top or bottom of the other nanoribbons.

The first results are concerned with the equilibrium structures at room (300 K) temperature. The purpose here is to verify the effects of thermal fluctuations on the structure of the system, without the application of any external constraint. As the graphene nanoribbons are
very pliable, it was verified if any deformation caused by thermal fluctuations lead the structures to change shape or configuration so becoming non-RS. Figure 3 shows these results for both equilibrated RSs and non-RSs. For the 3-fold RSs (top left panel of Figure 3), although the graphene nanoribbons are bent and curved, we can clearly see that the conditions for structural reciprocity continue to be satisfied, i.e., each nanoribbon sustains and is sustained by the others at different locations. Because of the reciprocity of the structure, the graphene nanoribbons did not fully overlap their surfaces due to van der Waals attractions. On the other hand, this happened with the 3-fold graphene-based non-RS shown in top right panel of Figure 3. The way the nanoribbons interact one to each other in non-RS due to its non-reciprocity allowed them to maximize the van der Waals interactions by twisting the ribbons out of the plane, so fully overlapping the surfaces close to the center of the structure. For the 4-fold structures, because they were already in a configuration of maximum overlapping of the nanoribbon surfaces, the equilibrated structures slightly differ regarding the initial configurations (shown in Figure 2) and between RS and non-RS.

Figure 3: Equilibrated graphene-based RSs (left column) and non-RSs (right column). The four insets show the whole structures, and the larger figures show their central parts in order to provide an enlarged view. Cyan (white) colors represent carbon (hydrogen) atoms.
The results for the mechanical impact tests are the most interesting from this study. Figure 4 shows the initial and final configurations for the projectile impact on the 3-fold (left panel) and on the 4-fold (right panel) graphene-based RSs (cyan color) and non-RSs (orange color). The figures are displayed to allow a direct comparison of the results. Videos showing the impact are provided in the Supplementary Information. The initial velocities given to the projectiles for the tests shown in Figure 4, were -20 and -30 Å/ps along z-direction, for the 3-fold and 4-fold cases, respectively. For the 3-fold case, smaller velocities did not lead to significant differences in the final results, while larger velocities caused the structural failures of both RS and non-RS. In the 4-fold case, smaller velocities did not cause significant differences in the final results for RS and non-RS. We can see from Figure 4 that for the 3-fold case, both RS and non-RS stopped the projectile. Regarding the impact test, we conclude that there was no mechanical advantage for the 3-fold RS. However, for the 4-fold case, the difference is remarkable. The graphene-based 4-fold RS was able to stop the projectile while the corresponding non-RS was not. This is a demonstration of the effectiveness of the structural reciprocity at nanoscale.

Figure 4: Initial (top row) and final (bottom row) configurations of the 3-fold (left side) and 4-fold (right side) of graphene-based RSs (cyan color) and non-RSs (orange colour). The initial velocities of the diamond projectile in each case were, in modulus, 20 and 30 Å/ps for the 3-fold and 4-fold cases, respectively. The lines indicate that some individual carbon atoms are ejected from the structure due to the impact and are scattered. Videos showing the full dynamics of the impacts are provided in the Supplementary Information.
We believe that for the 3-fold case, the reason for the non-RS to stand the same mechanical impact as the corresponding RS might come from the stability of the structure due to the large overlapping between the graphene nanoribbons. It would cost more energy to separate the nanoribbons surfaces in the 3-fold non-RS than for the original 3-fold RS. In other words, while the mechanical resistance for the 3-fold RS comes from the structural reciprocity features of the structure, for the 3-fold non-RS, the mechanical resistance comes from the maximized van der Waals overlapped nanoribbons structure.

This difference in surface overlapping does not occur for the 4-fold case. For both RS and non-RS 4-fold cases, the equilibrated structures possess about the same surface overlapping between the graphene nanoribbons. Thus, for this case, the difference in the mechanical resistance should come only from the structural reciprocity features. The results are shown in Figure 4.

There are also significant differences in the energy and stress profiles of the mechanical impact tests. For the 4-fold case where the difference in results for the mechanical test was significant, we have collected the potential energy and total stress values of the 4-fold structures during the impact.

In Figure 5, we present these results and we can clearly see that the potential energy and stress of the structures have different profiles during the mechanical impact tests. The RS is shown to absorb much more energy on its own structure than the non-RS. Also, interesting, the stress is released much faster for the RS than for the non-RS.

In summary, we presented the first computational study of the mechanical resistance at nanoscale of graphene-based da Vinci’s RSs. 3- and 4-fold RSs were built based on graphene nanoribbons and tools of molecular dynamics simulations were used to study the equilibrium configuration and the dynamics of the systems under ballistic impacts. Corresponding non-RSs were also studied for comparison. The results showed that 4-fold nanoscale RSs are more resistant than the corresponding non-RSs, even being formed by very pliable bars. These results might be of importance for applications such as nanotextiles made of graphene nanoribbons.
With relation to thermal stability, for the 3-fold RSs the conditions for structural reciprocity continue to be satisfied, although van der Waals forces tried to deform the structure by maximizing the overlapping between the graphene nanoribbons. Because of the reciprocity of the structure, the graphene nanoribbons were prevented from fully overlapping their surfaces, which happened to the 3-fold non-RS cases. For the 4-fold structures, because they were already in a configuration of maximum overlapping, the equilibrated structures slightly differ regarding their initial configurations for both RS and non-RS.

For the ballistic tests, there are not significant differences for RS and non-RS for the 3-fold structures. For the 4-fold cases there are significant differences. For some of the velocity values investigated here, RS were able to stop the projectile while the corresponding non-RS were
not. This is a demonstration that some of the da Vinci’s structural reciprocity concepts are still valid at nanoscale, even in the limit of absence of flexural rigidity of the bars that compose the structure.

One of the applications of RSs is related to building resistant bridges, domes, and roofs. Because of the low bending rigidity of graphene, it would not be useful for building mechanically resistant nano-bridges, but if, instead of graphene, we use for instance carbon nanotubes, those structures at nanoscale might be possible. Nanodomes might be built and be stable with high mechanical resistance. This might be of interest for creating isolated regions for reactions or nanoreactors. We hope the present results will stimulate further studies on the structural reciprocity-properties relationship at nanoscale.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information, details of author contributions and competing interests, and statements of data and code availability are available at http://…

References

1. Pugnale, A. & Sassone, M. Structural Reciprocity: Critical Overview and Promising Research/Design Issues. *Nexus Netw. J.* 16, 9-35 (2014).

2. da Vinci, L. *Il Codice Atlantico della Biblioteca Ambrosiana di Milano* (Giunti Editore, 2000).

3. Larsen, O. P. *Reciprocal Frame Architecture* (Architectural Press, Oxford, 2008).

4. Brenner, D. W., Shenderova, O. A., Harrison, J. A., Stuart, S. J., Ni, B. & Sinnott, S. B. A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. *J. Phys.: Condens. Matter* 14, 783-802 (2002).
5. Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Computational Phys.* **117**, 1-19 (1995).

6. LAMMPS - Molecular Dynamics Simulator. Available at http://lammps.sandia.gov (accessed 28 November 2019).

7. Yang, Y., Cai, K., Shi, J. & Xie, Y. M. Nanotextures from orthogonal graphene ribbons: Thermal stability evaluation. *Carbon* **144**, 81-90 (2019).

**Methods**

**Theory.** *Molecular dynamics (MD) simulations.* MD simulations were carried out using the AIREBO potential as implemented in LAMMPS computational package. In order to address the issue of mechanical resistance, we generated not only the 3- and 4-fold graphene-based RSs (right side of Figure 1) but also 3- and 4-fold graphene-based non-RSs as shown in Figure 2. The non-RSs were built by placing one or more graphene nanoribbons on top or bottom of the other nanoribbons, so breaking the rule of RSs of having each element of the structure supporting and being supported by the others. All graphene nanoribbons were Hydrogen passivated to avoid the formation of chemical bonds. The nanoribbons interact only via van der Waals interactions.

The structures are first geometry optimized by energy minimization methods (with force tolerance of 10-8 eV/Å) following by MD simulations at 300 K for, at least, 100 picoseconds using a Langevin thermostat. The time step and thermostat damping factor were set in 0.5 fs and 1 ps, respectively.

After thermal equilibration, all four structures shown in Figure 2 were subjected to impact mechanical tests. These tests consist of making parallelepiped diamond projectiles to collide with the RSs and non-RSs along their perpendicular direction and at their center. The parallelepiped diamonds have planar lateral sizes of 100 Å and thickness of 30 Å (thickness is measured along RSs perpendicular direction) and the effects of three different initial values of the velocities of
projectiles (10, 20 and 30 Å/ps) were investigated. The extremities of all graphene nanoribbons were kept fixed during the impact mechanical tests, and the rest of the RS or non-RS structures were thermostated (using Langevin thermostat at 300 K). Diamond projectiles were not thermostated. AIREBO was again considered to simulate the system including the interaction between the diamond projectiles and the RSs and non-RSs. The results are presented and discussed in the next section.

Acknowledgments

AFF and DSG are fellows of the Brazilian Agency CNPq. AFF acknowledges the grant #2018/02992-4 from São Paulo Research Foundation (FAPESP) and from FAEPEX/UNICAMP. DSG acknowledges the Center for Computational Engineering and Sciences at Unicamp for financial support through the FAPESP/CEPID Grant #2013/08293-7. This research also used the computing resources and assistance of the John David Rogers Computing Center (CCJDR) in the Institute of Physics “Gleb Wataghin”, University of Campinas.

Author contributions

A.F.F. conceived the project and performed the molecular dynamics simulations of the structures studied here. A.F.F. and D.S.G. analysed and discussed the results. The manuscript was written by A.F.F and D.S.G.

Competing interest

The authors declare no competing interests.