Tailoring Graphene to Achieve Negative Poisson’s Ratio Properties


Graphene, a one-atom-thick carbon allotrope featuring excellent mechanical, electronic, and thermal conductivity properties, is widely regarded as one of the possible wonder materials of the 21st century. Here, we show that its already remarkable properties may be further improved through modification of its nanostructure. In particular, negative Poisson’s ratio (auxetic behavior), that is the anomalous property of becoming wider rather than thinner when stretched, may be imparted to graphene at ambient conditions through the introduction of vacancy defects thus resulting in the thinnest auxetic material known so far with potential applications ranging from smart nanoelectromechanical devices to the design of nanocushions or nanodomes and smart nanofiltration. We indicate that this effect results from a de-wrinkling mechanism, which mimics the behavior exhibited by a crumpled sheet of paper when it is stretched.

Due to its unusual properties, graphene may well end up being used in various applications. In recent years, significant advances have been made in the design of devices utilizing graphene-based materials ranging from superior chemical and molecular sensors, to electronic equipment and nanoscillators. In fact, graphene is forecasted to be a potential replacement for a number of existing materials, especially if one is able to produce it with sufficient purity. As with other materials, the properties of graphene are highly dependent on the quality of the sample prepared. Prima facie, one might be concerned that the presence of defects will weaken the remarkable mechanical and electrical properties of this superstrong highly conductive ultrathin material, to the extent that it would become unusable in practical applications. However, it is known that in some cases, defects in graphene are beneficial and are introduced intentionally at the required size and concentration to bring about a desired quantified change in some property of graphene.

Materials with a negative Poisson’s ratio auxetics constitute another class of systems, which are becoming increasingly popular as a result of their remarkable properties. For example, it is now known that auxetics normally have the natural tendency to form dome-shaped conformations, i.e., synclastic curvature, which may be of use in the manufacture of curved body parts for aircrafts or automobiles. They also offer better indentation resistance when compared to their conventional counterparts, making them ideal for use in superior protective equipment. A number of materials and model systems have now been found to exhibit a negative Poisson’s ratio. These range from foams to single metal crystals and from model phases and macrostructures to nanomaterials. Despite recent works attempting to discover auxeticity in graphene-based and related carbon-based materials, a route to convert graphene to a material with significant auxetic characteristics at ambient conditions is still to be identified. In fact, prior art on the subject has dealt mainly with auxeticity in nanotubes or, in the case of single layer graphene, potential auxeticity at nonstandard conditions, such as very high temperatures or resonance under fully blocked boundary conditions with C–C bonds approximated by auxetic Timoshenko beams. Also, work reported so far which looked into the effect of vacancy defects on the Poisson’s ratio of graphene did not result in auxeticity, although the work by Dettori et al. did suggest a lowering of the Poisson’s ratio when vacancy defects at low concentrations are introduced.

This Communication presents the results of extensive molecular dynamics simulations that show how the conformation of graphene can be modified through the introduction of defects so as to make it amenable to exhibit a negative Poisson’s ratio.

In particular, molecular dynamics simulations at 300 K for different extents of uniaxial stress corresponding to a maximum of 10% uniaxial strain were performed upon systems having different concentrations of double vacancy defects of the 5–8–5 type (see Figure 1a and Supporting Information) which correspond to having p% of the atoms removed, where p% = 0.5%, 1.0%, 2.0%, and 3.0%. More specifically, a pristine graphene sheet having 28 800 carbon atoms, with dimensions ca. 25 nm × 29 nm was first constructed and positioned in the xy-plane with the armchair conformation being aligned parallel to the x-direction. As discussed in more detail in the Supporting
Information, standard periodic boundary conditions were applied in the y-direction while in the x-directions, some constraints on the atoms at the leftmost and rightmost edges were applied to permit loading and ensure that the system remains aligned in the xy-plane during the simulations. With these conditions, the structure being modeled corresponds to an infinite graphene nanoribbon, which can be stretched through a set of parallel rollers in the x-direction.

The defects were then generated by deleting 72, 144, 288, and 432 pairs of neighboring atoms (corresponding to 0.5%, 1.0%, 2.0%, and 3.0% of the atoms, respectively) in a random and nonoverlapping manner and then using a bond reconstruction process to ensure that all defects are truly of the 5–8–5 type. For each system, an energy expression was then set up using the adaptive intermolecular reactive empirical bond order (AIREBO) potential with periodic boundary conditions being used in the y-direction. Uniaxial loading was simulated by applying forces parallel to the x-direction on the atoms at the boundaries parallel to the y-direction. This procedure was used in an attempt to obtain a realistic graphene-like material, which could easily be studied under constant uniaxial stress conditions applied in the x-direction. Moreover, the atoms on which the stretching forces acted directly were further constrained so as not to move in the third direction. This was done so as to ensure that the graphene sheet behaves, as much as possible, as if it was gripped to horizontal rollers, i.e., similar to what happens in real-life mechanical testing. These constraints also ensure that the system remains parallel to the xy-plane throughout the simulation and also that the stress applied is purely uniaxial. These simulations were then repeated twice, to obtain three independent sets of results, each corresponding to different initial structures that have the same concentration of double-vacancy defects. Pristine graphene was also studied in order to ensure the reliability of the methodology used.

Typical images of the systems having various extents of defects in the unstretched state clearly suggest that as the extent of defects increases, the graphene sheets adopt a more wrinkled conformation thus achieving a shape which resembles that of a wrinkled paper model.
pulling in the paradigm that auxetic behavior necessitates the presence of a negative Poisson's ratio to be manifested. This further confirms the presence of particular geometric features, which are essential for a negative Poisson's ratio. It should be emphasized that the finding that graphene can be turned to an auxetic form simply through the introduction of defects at low concentrations (though not sufficient enough to result in a negative Poisson's ratio). At the same time, it indicates that some of the predictions made by Tapia et al. [27] based on a purely mechanical FEA-based model that vacancy defects increase the Poisson's ratio of defective hexagonal systems are not fully applicable to real graphene-like materials. This is probably due to the fact that the formulation of the model by Tapia et al. was not amenable to any crumpled conformation similar to the one reported here, conformation of which is essential for achieving a negative Poisson's ratio.

This is very significant as it suggests a clear route for turning regular conventional graphene to an auxetic form through the introduction of defects so as to produce one of the thinnest auxetic materials known so far which may be made to achieve tailored anomalous negative Poisson's ratio properties unattainable in pristine graphene under ambient conditions. However, this result should not be considered as a mere scientific curiosity, since it is obvious that the ability of converting graphene-like materials to an auxetic form is likely to result in a number of novel applications of this already exceptional material (e.g., enhanced nanoelectromechanical sensors, nanocushions, nanodomes, etc.) For example, the potential of using the imperfect graphene for making nanodomes can be easily demonstrated through the crumpled paper macromodel equivalent, which can be easily turned into a bowl-shaped conformation as opposed to its original noncrumpled form, which is much less amenable to adopting a synclastic curvature.

Before concluding, it is important to note that, despite the limitations one normally associates with force-field-based modeling studies, the work presented here provides a blueprint on how graphene and other sheet-like materials can be transformed to an auxetic state. Given the current level of experimental techniques used for modification of nanostructures, it is envisaged that the manufacturing and testing of such imperfect...
materials is not unlikely and may potentially lead to the production of a real manmade nanoscale auxetic material having truly multifunctional characteristics. Also, it is important to highlight that the discovery reported here, i.e., that crumpled sheet-like materials have the potential to exhibit a negative Poisson’s ratio is not only applicable solely to graphene with 5–8–5 type defects, but also to other similarly shaped materials, including membranes, for which a negative Poisson’s ratio has already been reported.\cite{30,33–35} It is also likely that imperfect graphene with other forms of defects at sufficiently high concentrations may also exhibit negative Poisson’s ratio.

To conclude, the work presented here shows, for the first time, how graphene can be modified to mimic the behavior of a highly and densely wrinkled paper model to the extent that it can exhibit auxetic behavior under ambient conditions. It is hoped that this result will stimulate further research in this field, especially work of an experimental nature, which should provide definite evidence that graphene with defects and structurally similar materials can assume a crumpled sheet conformation and indeed exhibit a negative Poisson’s ratio, with all the benefits that this brings with it. It is also hoped that this study will start to pave the way for a new gen-

Figure 3. The averaged in-plane Poisson’s ratios and Young’s moduli (calculated from the differential strains) plotted against the engineering strain for stretching in the $x$-direction as obtained from the simulations of pristine graphene ($p = 0.0\%$) and the imperfect graphene systems ($p = 0.5\%, 1.0\%, 2.0\%$, and $3.0\%$).
eration of products incorporating auxetic graphene, which would combine the useful properties associated with such a multifunctional materials from a mechano-electro-thermal point of view.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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