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CONDENSED MATTER

On the Vibrational Behavior of Graphynes and Its Family: a Molecular Dynamics Investigation

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Abstract Molecular dynamics (MD) simulation is used to investigate the vibrational behavior of γ-graphyne and its family. Five different nanosheet types including graphyne, graphdiyne, 3-graphyne, 4-graphyne, and 5-graphyne are considered for investigation. The fundamental natural frequencies of armchair and zigzag nanosheets with different geometrical sizes under different boundary conditions are computed. It is shown that increasing the size of γ-graphyne results in decreasing the natural frequency. Comparing the vibrational behavior of armchair and zigzag nanosheets, it is shown that for large nanosheets, the effect of atomic structure on the fundamental natural frequency can be neglected. Besides, it is represented that increasing the number of acetylene links connecting neighboring hexagons in the structure of nanosheets leads to decreasing the frequency.

Keywords Molecular dynamics simulations · Vibrational behavior · Graphyne

1 Introduction

Recently, the great properties of graphene have led to receiving the enormous scientific attraction to other 2D carbon allotropes. Being the most stable artificial and unnatural carbon allotrope [1], graphyne, which was proposed by Baughman et al. [2], can be considered as one of the most interesting 2D carbon allotropes. In addition to great mechanical and chemical properties [3–6], this novel carbon allotrope possesses unique electronic and thermal transport attributes [7–13].

In recent years, due to these unique properties which lead to their potential application in various fields, many researches have focused on different aspects of graphynes. The application of graphynes as molecular filters has been investigated by some authors. For example, Bartolomei et al. [14] used first-principle calculations to explore the interactions between water and graphyne, graphdiyne, and graphtriyne (3-graphyne) pores. They have shown that water transport is unfeasible through graphyne. Using molecular dynamics (MD) simulations, Kou et al. [15] showed that graphyne is impermeable to salt ions.

Employing MD simulations, Cranford and Buehler [3] have shown that the fracture stress and fracture strain of graphyne are in the ranges of 48.2 to 107.5 GPa and 8.2–13.2 %, respectively. Peng et al. [16] employed first-principle calculations to compute the mechanical properties of graphyne. They showed that while graphyne possesses a relatively low in-plane Young's modulus (162 N/m), it has a large Poison ratio (0.429) relative to grapheme. Qu et al. [17] investigated the mechanical and electronic properties of graphyne and its family under strain. They showed that increasing the number of triple bonds connecting two neighbor hexagons leads to reduction of in-plane stiffness.

Pei [18] used total energy calculation to compute the elastic parameters of graphdiyne. He showed that due to having less C–C bonds, graphdiyne is softer than graphyne. Yang and Xu [19] used MD simulations to determine Young's moduli of graphyne, graphdiyne, graphene-3, graphene-4, and graphene-5. Their results showed that these materials have large strength and stiffness. Salmalian et al. [20] used MD simulations to investigate the buckling behavior of graphyne and its family. They showed that the buckling forces of zigzag graphynes are larger than armchair ones.

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Besides, electronic properties of graphynes have been studied by different researchers. A nonzero band gap was found by Narita et al. [6] for graphyne and its families. Using first-principle calculations, Qu et al. [17] showed that the band gap of the graphyne family is modified by applying strain. Utilizing density functional theory (DFT), Majidi and Karami [21] have shown that the electronic properties of graphyne are not affected by the number of graphyne layer and configuration. Ouyang and Hu [22] showed that zigzag graphyne nanoribbons have superior thermoelectric performance than graphene.

Due to application of nanostructures in many nanomechanical devices such as oscillators, charge detectors, nanoscale clocks, field emission devices, and sensors [23], investigating their vibrational behavior is of great importance. Therefore, exploring the vibrational behavior of nanostructures, especially carbon nanotubes (CNTs), has become the subject of many scientific works in recent years [24–28].

Although the authors studied the instability of graphynes under compressive loads [20], a comprehensive study on their vibration has not been performed. So, in this paper, by employing MD simulations, fundamental natural frequencies of γ-graphyne and four other nanosheets from its family are computed. The influences of geometrical parameters on the fundamental natural frequency are investigated. Nanosheets are considered with six different boundary conditions. Moreover, the effect of chirality (being armchair and zigzag) on the nanosheet vibrational behavior is explored.

2 Models

In the structure of γ-graphyne and its family, the benzene rings are connected by single and triple (acetylene) links, alternatively. The number seen in the nanosheet name shows the number of acetylene links used to connect two neighbor hexagonal rings. Figure 1 shows a graphdiyne (2-graphyne) nanosheet. As it can be seen, the neighboring hexagons are connected by two triple bonds.

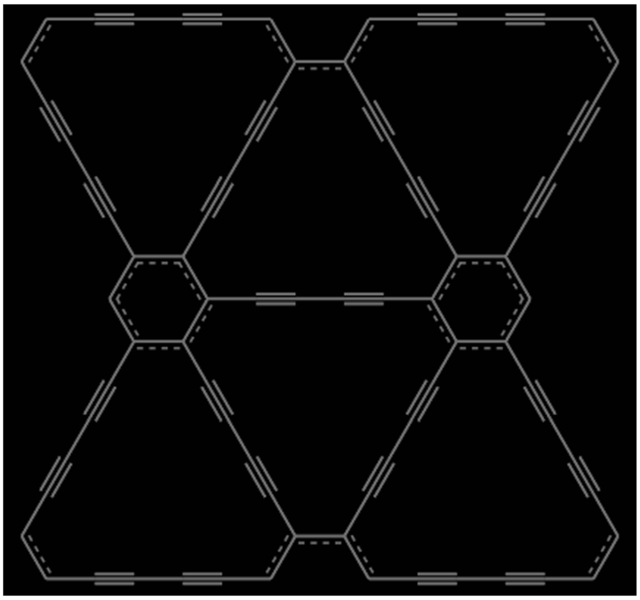


Fig. 1 A graphdiyne (2-graphyne) nanosheet in which neighboring benzene rings are connected by two acetylene links

3 Simulation Method

MD simulations are performed using LAMMPS MD code [29, 30]. The interactions between atoms are modeled using the adaptive intermolecular reactive empirical bond order (AIREBO) potential function [31]. This potential function, which has been developed to

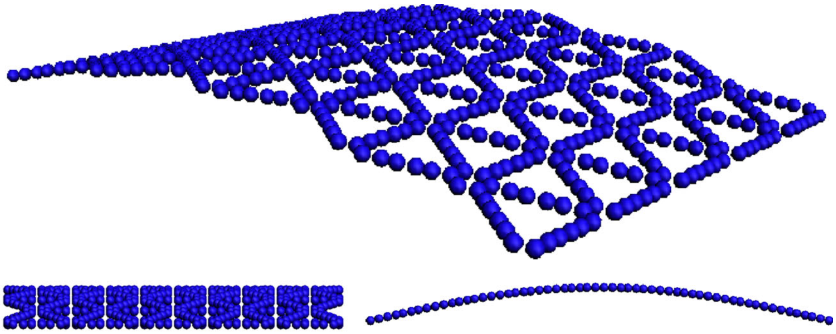


Fig. 2 A sample of displaced graphdiyne

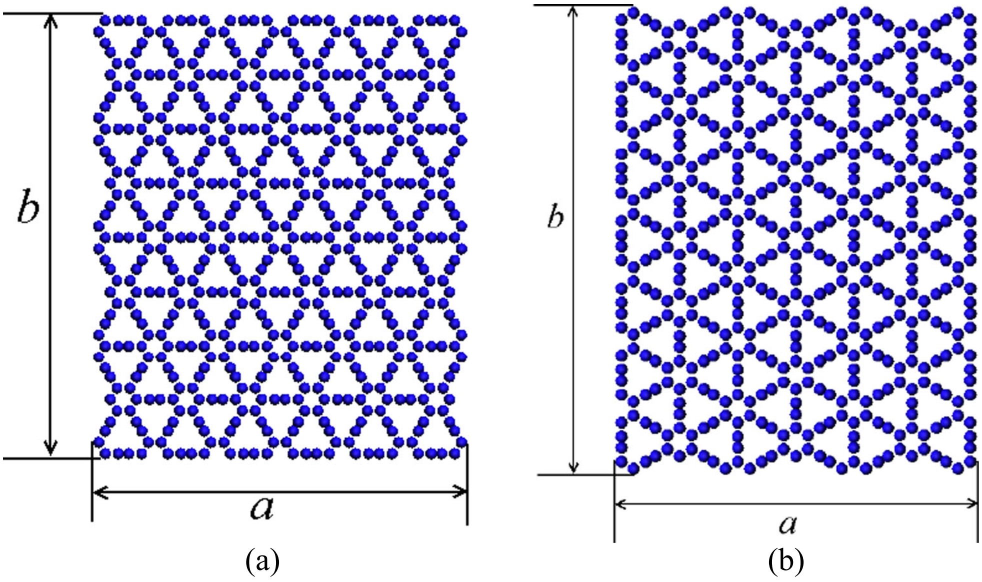


Fig. 3 **a** Armchair and **b** zigzag nanosheets with the associated geometrical parameters

describe the hydrocarbon structures, is the improved version of Brenner's second-generation reactive empirical bond order potential [32] by adding Lennard-Jones term to include van der Waals interactions, and torsional term to include torsions of σ bonds. Initially, the energies of systems are minimized and then using NVT (constant number of molecules, constant volume, and constant temperature) condition, the systems are relaxed for 20 ps. After that, the systems are let to vibrate. All of the equations are integrated with velocity Verlet algorithm [33]. Moreover, all of the time steps are considered as 1 fs.

4 Results and Discussion

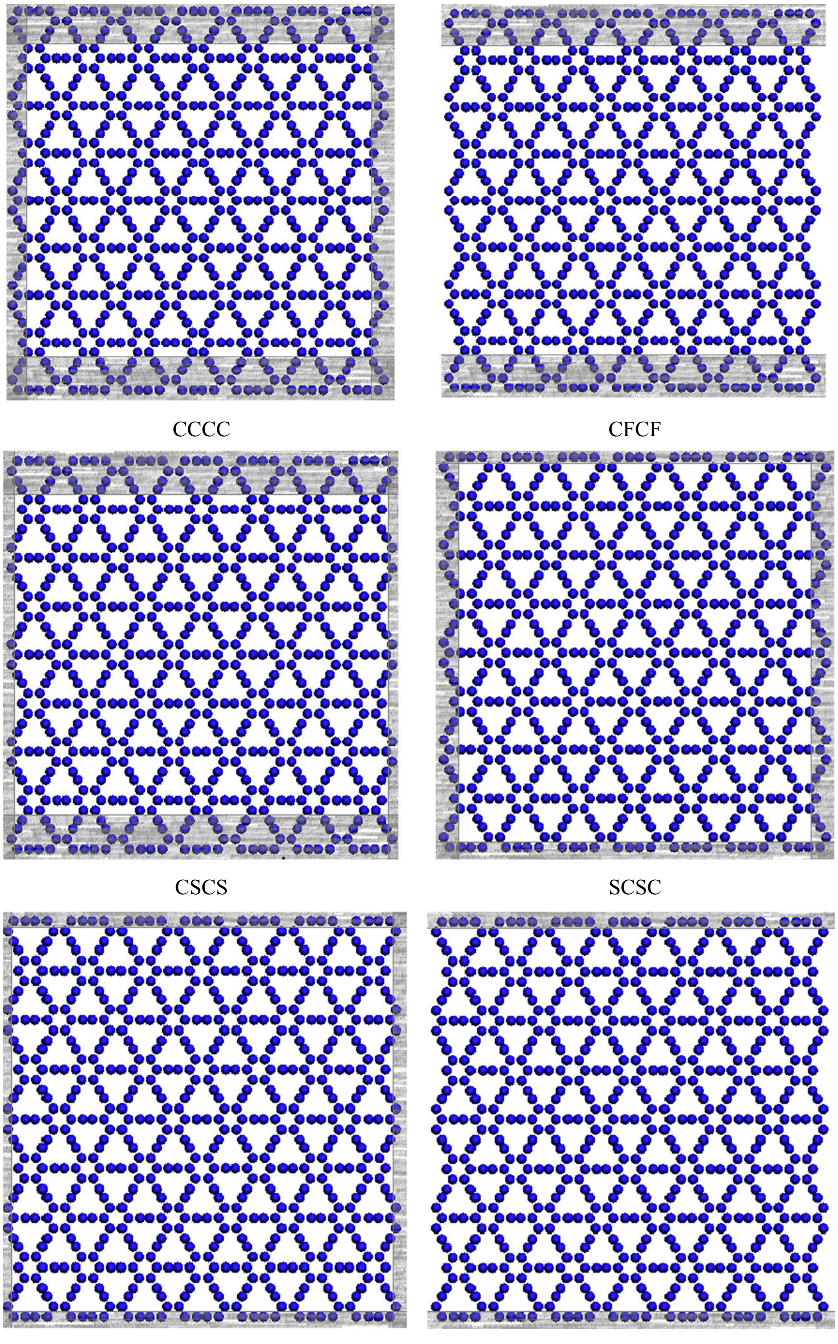
To explore the vibrational behavior, the nanosheets are put in their first mode shapes. The line of displaced atoms is parallel to top and bottom edges. Then, to obtain the frequencies of nanosheets, the systems are let to vibrate for 100 ps. A sample of displaced graphdiyne is shown in Fig. 2. Five different types of nanosheets from the graphyne family are selected for analysis including graphyne (graphyne-1), graphdiyne (graphyne-2), graphyne-3, graphyne-4, and graphyne-5.

The effects of geometrical parameters including side length (a in Fig. 3) and aspect ratio (b/a in Fig. 3) on the vibrational behavior of graphyne and its family are investigated. Chirality is another factor whose effect on the nanosheet fundamental natural frequency is studied. The armchair and zigzag nanosheets are represented in Fig. 3 with the associated geometrical parameters.

Besides, six different boundary conditions are considered as follows (the letters show top, right bottom, and left edges, respectively):

> Clamped-clamped-clamped-clamped (CCCC): All translational and rotational degrees of freedom of all four edges of nanosheets are constrained.
>
> Clamped-free-clamped-free (CFCF): All translational and rotational degrees of freedom of top and bottom edges are constrained and right and left edges are free.
>
> Clamped-simply supported-clamped-simply supported (CSCS): All translational and rotational degrees of freedom of top and bottom edges and translational degrees of freedom of right and left edges are constrained.
>
> Simply supported-clamped-simply supported-clamped (SCSC): Translational degrees of freedom of top and bottom edges and translational and rotational degrees of freedom of right and left edges are constrained.
>
> Simply supported-simply supported-simply supported-simply supported (SSSS): Translational degrees of freedom of all four edges of nanosheets are constrained.
>
> Simply supported-free-simply supported-free (SFSF): Translational degrees of freedom of top and bottom edges are constrained, and right and left edges are free.

Geometrically, for clamped boundary conditions, the motion of four rows of corresponding nanosheet side is restricted. Moreover, for simply supported boundary



CCCC CFCF

CSCS SCSC

SSSS SFSF

Fig. 4 Schematic of all of the simulated boundary conditions

conditions, only one row is constrained. The schematic of all of the simulated boundary conditions is shown in Fig. 4 for an armchair γ-graphyne.

Fundamental natural frequencies of armchair and zigzag γ-graphynes (graphyne-1) with different boundary conditions are given in Figs. 5 and 6 versus nanosheet aspect ratio. The side lengths of all of the sheets are chosen as 50 Å, and the aspect ratio varied from 0.5 to 3.

It is seen that increasing the aspect ratio results in decreasing the frequency. However, for the aspect ratios of 1.5 and larger than it, the effect of aspect ratio on

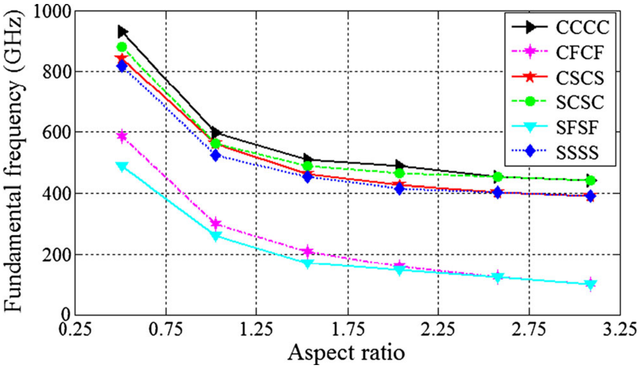


Fig. 5 Fundamental natural frequencies of armchair γ-graphynes (graphyne-1) with a side length of 50 Å under different boundary conditions

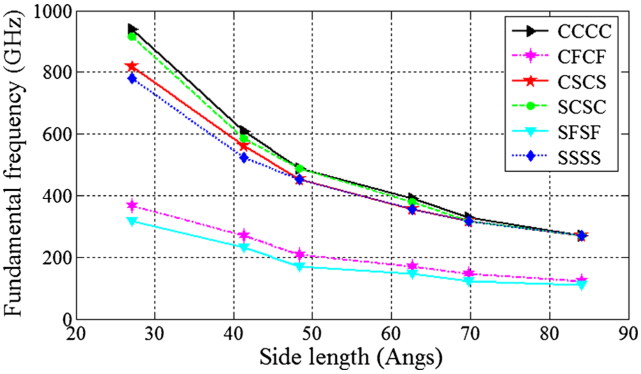


Fig. 7 Fundamental natural frequencies of armchair γ-graphynes (graphyne-1) with an aspect ratio of 1.5 under different boundary conditions

the vibrational behavior is too small. Besides, the order of frequencies from the largest to shortest is as follows: CCCC, SCSC, CSCS, SSSS, CFCF, and SFSF. The difference between curves decreases with increasing aspect ratio. As it is shown, for zigzag graphynes, the nanosheets under CCCC, SCSC, CSCS, and SSSS boundary conditions have the same frequency at the aspect ratio of 3.0. Comparing the curves associated with clamped boundary conditions with those of simply supported ones, one can conclude that the effect of constraining rotational degrees of freedom on the frequencies is small. This is especially observable for the CFCF and SFSF boundary conditions in which two curves coincide for the aspect ratios larger than 2.5.

The effect of side length on the fundamental natural frequencies of armchair and zigzag γ-graphynes is shown in Figs. 7 and 8. Again, six different boundary conditions are chosen. The aspect ratio of nanosheets is 1.5. It is observed that increasing the side length at a constant aspect ratio has an inverse effect on the graphyne frequency. This effect is too small for CFCF and SFSF boundary conditions. Besides, it is seen that for sufficiently large nanosheets, the effect of boundary conditions on the vibrational behavior of graphynes disappears. This is especially observable for zigzag nanosheets.

The effect of nanosheet structure on the fundamental natural frequency is observed in Fig. 9. The horizontal axes shows the number of acetylene links. As it was previously mentioned, the number of acetylene links connecting two neighboring hexagons determines the nanosheet name. So, 1, 2, 3, 4, and 5 triple links relate to graphyne, graphdiyne, 3-graphyne, 4-graphyne, and 5-graphyne, respectively. All of the nanosheets are selected with the side length of 70 Å and the aspect ratio of 2.5. It is seen that the largest frequency associates

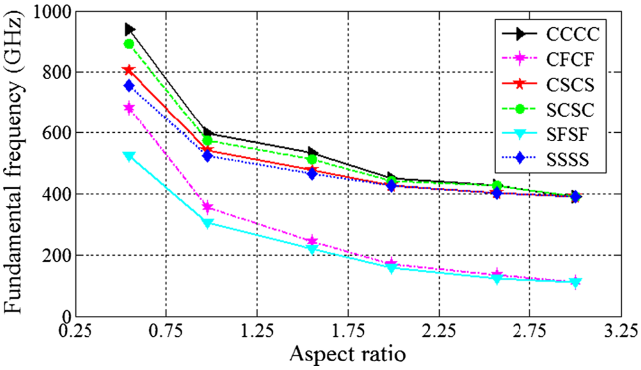


Fig. 6 Fundamental natural frequencies of zigzag γ-graphynes (graphyne-1) with a side length of 50 Å under different boundary conditions

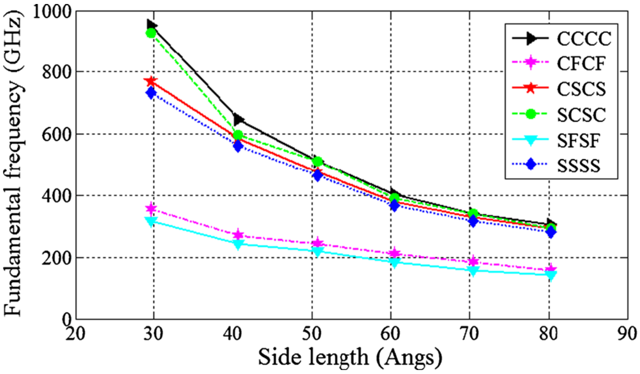


Fig. 8 Fundamental natural frequencies of zigzag γ-graphynes (graphyne-1) with an aspect ratio of 1.5 under different boundary conditions

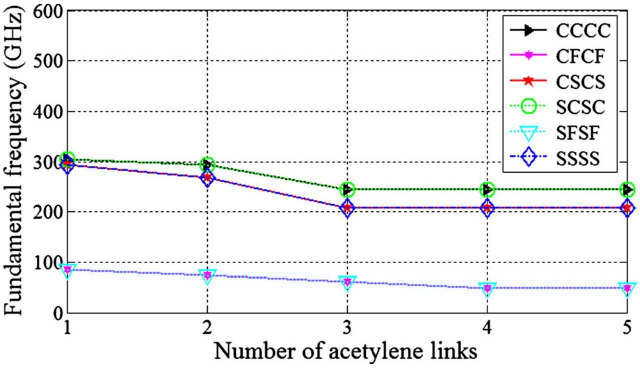


Fig. 9 Fundamental natural frequencies of armchair *n*-graphynes with a side length of 70 Å and an aspect ratio of 2.5 under different boundary conditions

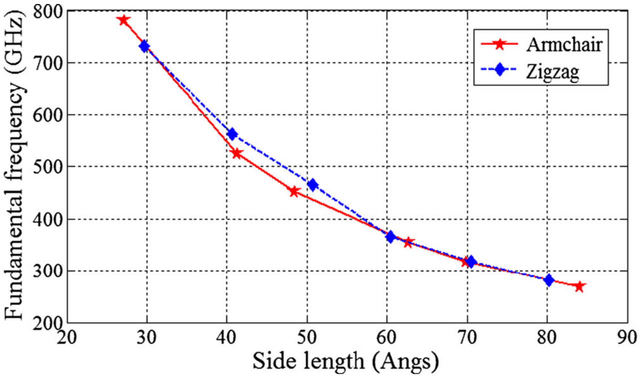


Fig. 11 Fundamental natural frequencies of armchair and zigzag γ-graphynes with an aspect ratio of 1.5 under SSSS boundary condition

with the graphyne with one triple link. In other words, the increasing number of acetylene links results in decreasing the frequency. The lowest influence of acetylene link on the vibrational behavior is for SFSF and CFCF end conditions. For all of the boundary conditions, after 3-graphyne, the curves take an almost linear form. Besides, it is seen that the curves of CCCC, CSCS, and CFCF coincide those of SCSC, SSSS, and SFSF boundary conditions, respectively. This observation reinforces the fact that for nanosheets of this size, the effect of rotational boundary conditions along the sides parallel to the displaced line of atom on the nanosheet vibrational behavior is not important.

Figures 10 and 11 show the effects of atomic structure on the fundamental natural frequency of γ-graphyne. In the first figure, the frequencies of CCCC armchair and zigzag nanosheets with the side length of 50 Å are plotted against the nanosheet aspect ratio and, in the second one, the frequencies of SSSS armchair and zigzag nanosheets with the aspect ratio of 1.5 are plotted against the nanosheet side length. It is seen that at the same geometrical size, the zigzag nanosheets possess higher frequencies than armchair ones. However, except for the initial part of Fig. 8, the difference is not significant. So, one can conclude that the influence of atomic structure on the vibrational behavior of nanosheets is only important for very small graphynes.

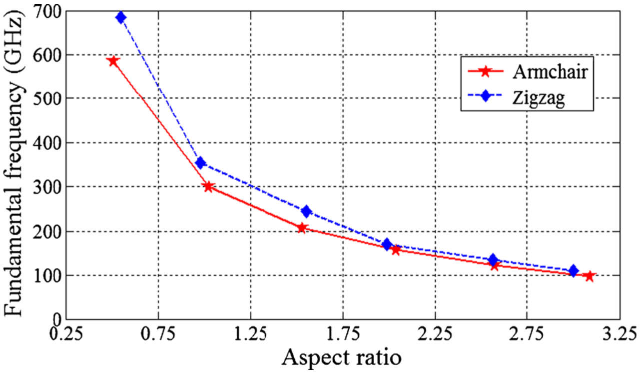


Fig. 10 Fundamental natural frequencies of armchair and zigzag γ-graphynes with a side length of 50 Å under CCCC boundary condition

5 Conclusion

Vibrational behavior of γ-graphyne and some types of nanosheets from its family including graphyne, graphdiyne, 3-graphyne, 4-graphyne, and 5-graphyne was explored. The effect of several parameters such as aspect ratio, side length, and end conditions on the fundamental natural frequency of nanosheets was studied. MD simulations were used to obtain the nanosheet frequencies. It was shown that increasing the side length and aspect ratio leads to decreasing the natural frequencies. Comparing the frequencies of armchair and zigzag γ-graphynes, it was observed that although for small nanosheets, zigzag graphynes have larger frequencies than armchair ones and, for large nanosheets, the effect of chirality disappears. The difference between different types of nanosheets from the graphyne family is in the number of triple bonds connecting two neighbor benzene rings. It was shown that with a larger number of triple bonds, nanosheets possess smaller frequencies.

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