Mechanical properties of hypothetical graphene foams: Giant Schwarzites

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Abstract

The mechanical properties of four different families of ordered porous graphene or giant Schwarzites, up to 12,288 atoms per cubic cell, were studied theoretically in order to shed light on the properties of newly synthesized graphene-like foams. It is shown that as the Schwarzite grows, the structure becomes flatter and not only more energetically stable, but also more elastically stable, thus opening the possibility of being synthesized in the near future. The mechanical properties such as bulk modulus, Young's modulus, and Poisson's ratio have been calculated with first principles for the smaller cells and with empirical methods for the larger cells. The bulk and Young moduli decrease as the structures grow. The "P" and the "I-WP" geometries favor smaller values of Poisson's ratio, likely to be synthesized experimentally. For the larger gyroid "G" and "D" cases, elastic instabilities appear, and these can be alleviated by breaking the symmetry of the associated space group. In addition, ripples in the graphene sheet stabilize the giant "D" family as the crystal cell dimensions increase. Finally, based on density functional theory calculations, the electronic properties of the high genus I-WP were examined for the first time finding semiconducting, semimetallic, and metallic behavior.

1. Introduction

Since the proposition of negative Gaussian curvature in graphitic systems through the introduction of carbon rings with more than six atoms, it was recognized the possibility of synthesizing negatively curved sp^2 -hybridized carbon, named Schwarzites, which exhibit topologies similar to those found in triply periodic minimal surfaces (TPMS) [1–3]. At that time, calculations showed the great stability and the diverse electronic properties of Schwarzites being insulators, semiconductors or metals [4]. The recent exciting properties found in experimentally synthesized graphene foams have brought back the challenging task of finding three dimensional graphene with similar features to Schwarzites [5].

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TPMS are a class of minimal surfaces, corresponding to zero mean curvature at every point, that are also periodic in three dimensions, and thus are crystalline. These surfaces all display non-positive Gaussian curvature since the two principal curvatures are opposite in sign and equal in magnitude, and exhibit saddle shapes at every point. In this paper, we examined four families of TPMS decorated with graphene, the Primitive (P), Diamond (D), Gyroid (G) and I-graph – Wrapped Package graph (I-WP) surfaces (see Fig. 1). The P ($Pm\bar{3}m - Im\bar{3}m$ space groups) and D ($Fd\bar{3}m - Pn\bar{3}m$ space groups) surfaces were first proposed by Hermann Schwarz [2, 6] and the G ($Ia\bar{3}d$ space group) and I-WP ($Pm\bar{3}m - Im\bar{3}m$ space groups) were later proposed by Alan Shoen [7]. Small and giant Schwarzites exhibit similar topologies and space groups as the TPMS, however, giant Schwarzites such as the ones we are studying here, are more graphenic in the sense that the ratio of hexagons to rings with more than six atoms, is very high, so are locally flat. Very little has been discussed about the properties of these giant Schwarzites, mainly due to the lack of experimental evidence and the difficulties to generate and deal with large number of atoms in theoretical calculations. In this paper we generate and study the mechanical properties of giant Schwarzites up to 12288 atoms per cubic cell. These calculations might help in understanding the newly synthesized graphene foams [5, 8] and to predict novel graphenic arrangements in three dimensions.

One of the most exciting properties of graphene, a single layer sheet of graphite, is its unique linear energy dispersion close to the K points in the Brillouin zone forming Dirac cones, in which electrons behave as Dirac Fermions [9–11]. This behavior has been recently found theoretically in a gyroid “G” Schwarzite with 1536 atoms in the cubic cell, exhibiting hyper Dirac cones in the valence and conduction bands which can be shifted to the Fermi level by lithium doping [12]. In this context, electronic properties of smaller Schwarzites have been studied and no Dirac Fermion behavior has been found. However, they can be metals, semimetals, semiconductors or insulators depending on their geometry and their size [4]. This diversity in electronic behavior with sp^2 -hybridized carbon atoms, in addition to the newly observed Poisson ratio close to zero in a graphene foam [5], justifies the current study on giant Schwarzite systems not reported hitherto.

In this paper, we computed 35 Schwarzites based on D, G, P and I-WP TPMS using density

Figure 1: A single cubic cell of the (a) D, (b) P, (c) G, and (d) I-WP minimal surfaces.

functional theory (DFT) and empirical methods: The energetics, elastic stability and mechanical properties such as Young modulus, bulk modulus and Poisson ratio were calculated. Emphasis has been put on giant Schwarzites that have not been studied before. We also calculated for the first

time, using DFT, the electronic structure for the smallest cases of the I-WP structures finding that they exhibit semi-metallic, metallic and semi-conducting behavior depending on size. We found that the giant P and I-WP Schwarzites can be grown preserving the topology and symmetry (space group), and this is not the case for the giant G and D Schwarzites that require the space group symmetry to be broken or the presence of ripples to be elastically stable. With the term “grow” we mean that the structure can be “inflated” by the addition of hexagonal rings, thus preserving the number of rings with more than six carbon atoms, such as octagonal carbon rings. In other words, the Schwarzites we have studied are formed by varying the number of hexagons with a fixed number of octagons. We found that the P giant Schwarzites exhibit the lowest average Poisson ratios around 0.183. If defects, such as ripples, are considered, it is possible to lower the Poisson ratios as we will see for the D giant Schwarzites.

2. Methods

2.1. Generation of Schwarzites with Surface Evolver

In a decorated TPMS using only hexagonal and octagonal rings, it is possible to derive the number of octagons that should be present through the Gauss-Bonnet theorem as shown in Eq. 1 where “ g ” is the genus per primitive cell and N_5 , N_7 and N_8 are the number of pentagons, heptagons and octagons, respectively, present in the Schwarzite [2]. It can be easily verified that the P, D, and G surfaces with genus equal to 3 will have 12 octagons in the primitive cell and the I-WP surface, with genus per primitive cell equal to 4, will have 18 octagons in the primitive cell. Given an initial continuous surface patch for each surface, the Surface Evolver code [13] was used to calculate each decorated surface with carbon atoms associated to a TPMS, and then to increase the size of the structure. For the initial patch for each surface the octagonal rings are located in the region with the greatest magnitude in Gaussian curvature. For the I-WP, the location of some octagons was also determined to preserve the symmetry of the surface. Surface Evolver calculates the local minimum of a specified energy functional iteratively using a gradient descent method [13]. For our purposes, that energy was calculated by minimizing a weighted sum of the surface area, the squared mean curvature, and the deviation of the atomic separation. Finally, the center

of each facet in Surface Evolver is used as the location of an atom on the calculated surface. See Fig. 2 as an example of an overlay of the decorated surface on the calculated surface.

$$N_5 - N_7 - 2N_8 = 12(1 - g) \quad (1)$$

Through the use of Surface Evolver we have generated all the initial coordinates for each of the four families studied. Each family contains two sub-families, the normal calculated surface and a second set referred as rotated structures. In these rotated structures, the octagonal rings are rotated by $\pi/4$ radians which results in a rotation of the hexagonal rings by $\pi/3$ radians as well as a change in the number of hexagonal rings. Each calculated Schwarzite is named using the following convention. First the abbreviated letter of the surface (P,D,G or I-WP), next an “8” referring to the introduction of octagonal rings, followed by the minimum number of hexagonal rings separating two octagonal rings. Lastly, “Rot” is appended in the case of the rotated sub-family (ex. P8-5 or D8-11Rot). Figure 3 shows the difference between the P8-1 structure and the associated rotated P8-2Rot structure.

2.2. Computer Simulations

The elastic properties of the porous graphene have been calculated considering different cubic cells using the Brenner reactive empirical bond order (REBO) potential [14] with the code GULP (general utility lattice program) [15]. For the smallest structures, a first principles plane wave DFT approach coded in CASTEP [16] has been used, finding a good agreement between the mechanical properties of GULP and CASTEP. For the first principles calculations, cubic cells were considered under the Local Density Approximation (LDA) using the Ceperly-Alder-Perdew and Zunger (CA-PZ) functional [17, 18] with variable Monkhorst-Pack K-points, depending on the size (3x3x3 for the I-WP cases), and a plane waves cut off of 500 eV with a norm-conserving pseudopotential. All the structures were relaxed, including the cells, until the forces became smaller than 0.05 eV/Å and with self-consistent energy tolerances less than 2×10^{-5} eV/atom. For consistency, all the values of the mechanical properties given in the tables of this paper have been calculated with GULP.

Figure 2: Overlay of the decorated structures on the calculated surfaces using Surface Evolver. All structures shown are of the 8-1 variety. Cubic cells are displayed for (a) the D8-1, (b) the P8-1, (c) the G8-1, and (d) the I-WP8-1.

Figure 3: Molecular models of: (a) the decorated P8-1 and (b) the P8-2Rot structures. Each structure is displayed as two cubic cell side by side. The octagonal rings in the P8-2Rot have been rotated by $\pi/4$ radians and the hexagonal rings have been rotated by $\pi/3$ radians. Pictured above each structure is the orientation of the octagonal rings. The P8-2Rot has only 144 atoms per cubic cell compared to the P8-1 which has 192 atoms per cubic cell. The scale bar in the bottom left corner of each represents 1 Å.

3. Results

3.1. Energetics

The calculated energetics using the REBO potential (energy per/atom relative to graphene) for all structures examined are shown in Fig. 4. The results obtained for the smaller structures examined from the P, D, and G families agree relatively well with previous calculations reported in the literature [4, 19], but there are no values available to compare for our giant cases up to 12,288 atoms per cubic cell. Of the four families analyzed, the P family most closely approaches the energy per atom of graphene as increasing the lattice parameter. The I-WP family also approaches low energy values similar to graphene but has much higher energies for the smallest cells. While the G family approaches energetics similar to graphene, structures from this family also display elastic instabilities for larger sizes which do not satisfy the Born criteria [20] (see below). The G8-7 Schwarzite was elastically unstable when symmetrically constrained following the $Ia\bar{3}d$ space group. This structure and the G8-23Rot were instead calculated without constraint to symmetry in order to find a more elastically stable structure. We believe that the instability of the giant Gyroids come from the fact that the G TPMS does not contain straight lines and graphene prefers to keep its flatness by possessing straight lines. The D surface family is interesting as the energies do not change much as the size of the cell grows. The addition of hexagons to this family of Schwarzites

Figure 4: The energetics of Schwarzites relative to graphene. A value of 0eV per atom is the energetics of graphene calculated using the Brenner empirical potential.

seems to have no effect on lowering the energetics towards that of graphene. In addition, the largest of the D Schwarzites (D8-15 and D8-23Rot) both display ripples as we will discuss latter in detail.

Of the four families of Schwarzites examined here, the P and I-WP families look the most promising to be synthesized since they display energetics that approach that of single layer graphene while remaining elastically stable. Also, from the relaxed structures, there are large patches on the largest structures that appear to closely resemble flat graphene layers. The P8-15 displays flat hexagonal regions that are connected at the octagonal sites (see Fig. 5). The I-WP8-15, with more octagons per cubic cell than the P family, displays quadrilateral regions that are also flat (see Fig. 6).

3.2. Elastic properties

For all structures with cubic symmetry the elasticity tensor contains only three unique values, c_{11} , c_{12} , and c_{44} (see Table 1). The same holds for the compliance tensor, which is the

Figure 5: A single cubic cell of the P8-15 structure (a) before relaxation and (b) after relaxation. The hexagonal regions with low curvature are now even flatter as they become more graphenic. Of all the structures examined in this paper, this structure has energetics closest to graphene. The scale bar in the lower left corner is for $10\text{\AA}$.

Figure 6: A single cubic cell of the I-WP8-15 structure (a) before relaxation and (b) after relaxation. Here, there are quadrilateral regions that become flat and graphenic. The scale bar in the lower left corner is for $10\text{\AA}$.

inverse of the elasticity tensor with values: s_{11} , s_{12} , and s_{44} . In 1940 Max Born established the conditions for elastic stability in cubic lattices as listed in Eq. 2 [20, 21].

Given the cubic elastic constants and the corresponding values from the compliance tensor, average values for Young's modulus and Poisson's ratio were calculated. These values refer to the macroscopic effective value for each quantity. Equations 3 and 4 provide the Voight average for Young's modulus and Poisson's ratio [22]. This value is at the upper bound for Young's modulus and a lower bound for the Poisson's ratio. Equations 5 and 6 give the Reuss average for these two quantities. In this case, the value is a lower bound for Young's modulus and an upper bound for Poisson's ratio. Equation 7 gives the Voigt-Reuss-Hill average for Young's modulus while Eq. 9 provides the Voigt-Reuss-Hill average for the Poisson's ratio, which requires calculating the Voigt-Reuss-Hill average for the shear modulus given in Eq. 8. These equations are all described by Toonder, Dommelen, and Baaijens [22]. Figures 7 and 8 shows the values of the Voigt-Reuss-Hill average for both quantities.

$$c_{11} - c_{12} > 0 ; c_{11} + 2c_{12} > 0 ; c_{44} > 0 \quad (2)$$

$$E_V = \frac{(c_{11} - c_{12} + 3c_{44})(c_{11} + 2c_{12})}{c_{11} + 3c_{12} + c_{44}} \quad (3)$$

$$\nu_V = \frac{c_{11} + 4c_{12} - 2c_{44}}{4c_{11} + 6c_{12} + 2c_{44}} \quad (4)$$

$$E_R = \frac{5}{3s_{11} + 2s_{12} + s_{44}} \quad (5)$$

$$\nu_R = -\frac{2s_{11} + 8s_{12} - s_{44}}{6s_{11} + 4s_{12} + 2s_{44}} \quad (6)$$

$$E_{VRH} = \frac{E_V + E_R}{2} \quad (7)$$

$$G_{VRH} = \frac{1}{2} \left[\frac{c_{11} - c_{12} + 3c_{44}}{5} + \frac{5}{4s_{11} - 4s_{12} + 3s_{44}} \right] \quad (8)$$

$$\nu_{VRH} = \frac{E_{VRH}}{2G_{VRH}} - 1 \quad (9)$$

In addition to the average values of Young's modulus and Poisson's ratio calculated from the elastic constants, these quantities were calculated in the [100] direction of the cubic cell. These

Figure 7: Averaged Poisson's ratio of graphene foams as the size of the cubic cell grows. The calculated average Poisson ratio can increase or decrease for each Schwarzite. The D8-23Rot displays a negative Poisson ratio.

Figure 8: Averaged Young's modulus of graphene foams as the size of the cubic cell grows. The averaged Young's modulus ranges from 358 GPa (I-WP8-0) to 5.96 GPa (P8-15).

values can be found in Table 2. The P family displays the highest values for the Poisson's ratio ranging from 0.408 to 0.353 along the direction [100]. However, for the same structures from the P family, the averaged value for the Poisson's ratio of the entire cubic cell is smaller for all cases, so that the P8-15 displays an average value of 0.183 (see Fig. 7).

In contrast to the P family, the I-WP family displays the smallest values of the Poisson's ratio calculated in the [100] direction. However, for this family the average values of the Poisson's ratio is always larger than the Poisson's ratio along the [100] direction. Consequently, the averaged values for the I-WP family are typically similar or larger than those for the P family. In addition, for larger structures in the I-WP family the value of the Poisson's ratio increases as the lattice parameter increases (See Fig. 7). It is worth mentioning here that the D Schwarzites with ripples D8-15 and D8-23Rot possess average Poisson ratios of 0.195 and -0.063, respectively (see Figs. 9, 10 and Table 2). Note the negative value for the D8-23Rot case, thus ripples might play a role in contributing to lower the Poisson ratio of graphenic structures.

Table 1 does not include the G8-7 and the G8-11Rot Schwarzites, since these structures do not possess cubic symmetries after the relaxation since the cubic symmetry needs to be broken to find a more stable system (See Fig. 11). Also, for the I-WP8-15 and the I-WP8-23Rot, the primitive cell was used for the calculations, not the cubic cell, due to the large number of atoms present in the cubic cell (the primitive cell of a body centered cubic cell possesses half of the atoms of the cubic cell). For these structures the values for elastic properties are given in Table 3.

3.3. *Electronic Structure of the I-WP*

The electronic structure for small cases from the non-rotated genus three P, D, and G families has been studied [4]. However, there has not been work done on structures from the I-WP family which exhibits genus 4 per primitive cell. Here, we examined using DFT the I-WP8-0 (96 atoms per cubic cell), the I-WP8-1 (384 atoms per cubic cell), and the I-WP8-2Rot (288 atoms per cubic cell) Schwarzites. The I-WP8-0 Schwarzite is unique in the sense that it does not contain any hexagonal rings of carbon in its smallest case, while preserving the sp^2 hybridized bonding possessing only octagonal rings (see Fig. 12). This structure displays a density of states showing a semi-metallic behavior that resembles graphene (see Fig. 13). The calculations reveal that the

Structure	n	a	ρ	c_{11}	c_{12}	c_{44}	K
D8-0	24	6.063	2.147	313.89	215.51	117.66	248.31
D8-1	96	11.724	1.187	220.68	90.35	64.54	133.80
D8-3	384	23.148	0.617	99.78	41.57	9.40	60.97
D8-7	1536	45.990	0.314	42.06	14.78	13.79	23.87
D8-15 ^a	6144	90.370	0.166	10.16	3.59	5.41	5.78
D8-2Rot	72	9.900	1.479	267.80	97.21	81.28	154.07
D8-5Rot	288	20.110	0.705	129.77	49.41	23.37	76.20
D8-11Rot	1152	40.030	0.358	54.33	20.01	22.16	31.45
D8-23Rot ^a	4608	78.760	0.188	55.54	-16.03	5.51	7.82
P8-0	48	7.800	2.017	268.92	185.64	59.02	213.40
P8-1	192	14.911	1.155	147.31	99.32	79.83	115.32
P8-3	768	29.020	0.626	54.74	34.38	43.24	41.17
P8-7	3072	56.920	0.332	20.50	11.52	19.27	14.51
P8-15	12288	112.570	0.171	8.13	4.44	7.71	5.67
P8-2Rot	144	12.984	1.311	168.87	114.10	80.70	132.36
P8-5Rot	576	25.251	0.713	67.82	43.90	44.59	51.88
P8-11Rot	2304	49.463	0.379	25.15	14.65	21.67	18.15
P8-23Rot	9216	97.767	0.197	9.80	5.40	9.16	6.87
G8-0	96	9.601	2.163	315.10	202.80	90.77	240.24
G8-1	384	18.411	1.227	195.16	90.73	68.49	125.54
G8-3	1536	35.711	0.672	58.63	21.56	24.77	33.92
G8-7 ^b	6144	69.331	0.367	-32.32	26.10	-23.49	6.63
G8-2Rot	288	16.030	1.394	219.83	107.42	86.39	144.89
G8-5Rot	1152	31.110	0.762	81.74	26.19	35.17	44.70
I8-WP-0	96	9.528	2.212	404.94	109.36	36.75	207.89
I8-WP-1	384	18.148	1.281	235.75	50.20	40.55	112.05
I8-WP-3	1536	34.800	0.726	84.29	15.33	15.37	38.32
I8-WP-7	6144	67.140	0.404	25.79	5.73	3.71	12.42
I8-WP-2Rot	288	15.904	1.427	253.60	70.76	29.56	131.71
I8-WP-5Rot	1152	30.460	0.812	95.39	22.23	15.74	46.62
I8-WP-11Rot	4608	58.590	0.456	31.71	6.72	4.08	15.05

Table 1: Table of the calculated mechanical properties for all cubic cases of Schwarzites examined in this paper. The number of atoms per cubic cell (n) is given in addition to the lattice parameter (a) given in angstroms. The density (ρ) is given in g/cm³. The elastic constants (c_{11} , c_{12} , & c_{44}), the bulk modulus (K), and Young's modulus (Y_{100}), given perpendicular to the cubic faces, are given in GPa. Lastly, is the Poisson's ratio (ν_{100}), given perpendicular to the cubic faces.

^aThese structures exhibits ripples when relaxed

^bThe G8-7 when constrained to the $Ia\bar{3}d$ space group is not elastically stable according to Eq. 2.

Structure	Y_{100}	Y_{avg}	ν_{100}	ν_{avg}
D8-0	138.434	223.699	0.407	0.349
D8-1	168.188	167.346	0.290	0.292
D8-3	75.331	41.749	0.294	0.384
D8-7	34.373	34.564	0.260	0.259
D8-15 ^a	8.291	10.586	0.260	0.195
D8-2Rot	216.028	210.811	0.266	0.272
D8-5Rot	102.529	77.392	0.275	0.331
D8-11Rot	43.566	49.520	0.269	0.238
D8-23Rot ^a	42.527	24.315	-0.405	-0.063
P8-0	117.291	142.535	0.408	0.389
P8-1	67.321	129.354	0.402	0.309
P8-3	28.226	60.715	0.385	0.243
P8-7	12.214	25.811	0.359	0.191
P8-15	4.997	10.368	0.353	0.183
P8-2Rot	76.866	138.557	0.403	0.323
P8-5Rot	33.315	67.461	0.392	0.276
P8-11Rot	14.376	30.015	0.367	0.213
P8-23Rot	5.960	12.371	0.355	0.188
G8-0	156.281	203.455	0.391	0.359
G8-1	137.580	158.476	0.317	0.290
G8-3	47.035	54.380	0.268	0.233
G8-2Rot	149.300	186.870	0.328	0.285
G8-5Rot	69.030	77.504	0.242	0.211
I8-WP-0	358.420	180.415	0.212	0.349
I8-WP-1	218.120	145.844	0.175	0.282
I8-WP-3	79.570	54.042	0.153	0.264
I8-WP-7	23.710	14.581	0.181	0.302
I8-WP-2Rot	222.720	126.753	0.218	0.337
I8-WP-5Rot	86.980	57.498	0.189	0.293
I8-WP-11Rot	29.360	17.042	0.175	0.308

Table 2: Table of Young’s moduli and Poisson’s ratios for all elastically stable, cubic cases of Schwarzites examined in this paper. The Young’s modulus (Y), given in GPa, is listed perpendicular to the cubic faces (in the [100] direction) or as the macroscopic averaged values. The Poisson’s ratio (ν) is also given perpendicular to the cubic faces and as the macroscopic averaged value.

^aThese structures exhibits ripples when relaxed

Structure	a	ρ	K	Y_x	Y_y	Y_z	ν_{xy}	ν_{xz}	ν_{yx}	ν_{yz}	ν_{zx}	ν_{zy}
G8-7	$a = 67.35$ $b = 70.24$ $c = 67.10$ $\alpha = 90.71$ $\beta = 89.00$ $\gamma = 90.64$	0.39	4.52	8.24	23.00	8.50	0.230	-0.050	0.080	0.040	0.050	0.127
G8-11Rot	$a = 58.95$ $b = 60.76$ $c = 58.95$ $\alpha = 89.51$ $\beta = 91.08$ $\gamma = 90.48$	0.44	5.62	8.30	23.32	8.18	0.140	0.260	0.050	0.050	0.270	0.160
I-WP8-15	131.05	0.22	3.11	2.70	3.03	3.03	0.398	0.398	0.355	0.355	0.274	0.274
I-WP8-23Rot	114.03	0.25	4.46	2.84	3.32	3.32	0.458	0.458	0.393	0.293	0.393	0.293

Table 3: Table of the calculated mechanical properties for all special cases of Schwarzites examined in this paper. This includes cases without cubic symmetry or cases where the primitive cell was used as a result of the large number of atoms in the cubic cell. The lattice parameter for non-cubic cases is given for all three dimensions and includes the angles of the cell. In all cases, the lattice parameter is given in angstroms while the angles are given in degrees. The density (ρ) is given in g/cm³. The bulk modulus (K) and the Young's modulus, given in three directions (Y_x , Y_y , and Y_z), are all given in GPa. Lastly, Poisson's ratio (ν) is given with two indices, the first referring to the direction of stress being applied and the second referring to the direction of expansion or contraction.

Figure 9: The front half of the cubic cell of the D8-15 structure (a) before relaxation and (b) after relaxation. The scale bar in the lower left corner is for $10\text{\AA}$.

Figure 10: Two cubic cells of the D8-23Rot structure. This variation of the structure displays ripples in the hexagonal regions with lower curvature. While this structure has slightly higher energetics when compared to the relaxation without ripples (see Fig. 4) the averaged Poisson's ratio is predicted to be negative (see Fig. 7). The octagonal rings that lie on the boundary of the surface are not complete as some of the atoms lie in the next cubic cell. The scale bar in the lower left corner is for $10\text{\AA}$.

Figure 11: A single cubic cell of the G8-7 structure (a) before relaxation compared to (b) after relaxation without constraint to the $Ia\bar{3}d$ space group. This structure still contain a symmetric point of inversion in the center. It can be seen that the structure becomes distorted as small regions become more graphenic when relaxed. This structure is elastically stable unlike the other relaxation of the G8-7 and also has slightly lower energetics in comparison (see Fig. 4). The scale bar in the lower left corner is for 10Å.

Figure 12: A single cubic cell of the relaxed IWP8-0 structure. This structure only contains octagonal rings. The octagonal rings parallel to the cubic faces appear flat while the octagonal rings along regions of higher curvature are more distorted. The scale bar in the bottom left represents 1Å.

slightly larger I-WP8-1 Schwarzite is a semiconductor with an indirect band gap calculated, to be 0.866 eV, and the I-WP8-2Rot, which lies in size between the I-WP8-0 and the I-WP8-1, exhibits metallic behavior. From these results we conclude, that the electronic properties involve a variety of behaviors, depending on the size. What remains an open question is if by increasing the size, hyper Dirac cones can be found as in the case of one the G Schwarzites [12].

4. Conclusion

The mechanical properties of new giant Schwarzites have been calculated in order to shed light on the observed properties of the experimentally synthesized graphene foams. Regarding the stability of these periodic sp^2 carbons, we have gone further than just considering the energetics, and also consider the elastic stability by satisfying the Born criteria.

For all the elastically stable cases studied, the Young modulus decreases as the size of the Schwarzite increases. Poisson's ratios calculated are not as low as those found by Wu, Y. et. al. in experimentally produced graphene foams from graphene oxide [5]. We believe that this might be due to the defects present in graphene oxide. In fact, one of the models used by Wu, Y. et. al. is similar to one of the I-WP cases studied here, but containing defects such as pentagonal and additional octagonal rings. Thus, further work should examine the introduction of topological

Figure 13: Band structure and density of states for (a) the I-WP8-0, (b) the I-WP8-1 (top right), and (c) the I-WP8-2Rot (bottom center) Schwarzites. For the I-WP8-0 there are multiple locations of crossing at the Fermi energy near the Γ and H points in the Brillouin zone. The density of states appears similar to that of single layer graphene. The I-WP8-1 structure has an indirect gap of 0.866 eV near the P and N points in the Brillouin zone. Lastly, the I-WP8-2Rot appears to be metallic from the density of states.

defects in these giant Schwarzites. In addition, from our results we found that as the structures grows, ripples are formed that can also form re-entrant surfaces that could cause a decrease in the Poisson's ratio. We showed that for the giant D Schwarzite with ripples, the Poisson ratio decreases and becomes negative. Negative Poisson ration materials out of graphene constitute a fascinating possibility that needs further experimental studies.

Defects also play an important role in the mechanical and electronic properties of graphene. Two primary defects have been previously considered, Stone-Thrower-Wales (STW) defects, involving a bond rotation to create two heptagonal and two pentagonal rings, and divacancy defects, the removal of two atoms to form two pentagonal rings and an octagonal ring [8]. Carlsson and Scheffler have shown that in small concentrations STW defects are stable [23]. Grima et. al. found that introducing divacancy defects onto single layer graphene results in a negative Poisson's ratio [24]. In this contex, Dettori, Cadelano, and Colombo have shown a decrease in the Poisson's ratio through the introduction of STW defects in graphene [25].

Another result we found is that as the gyroid Schwarzites grow around 6144 atoms per cubic cell, the structures become elastically unstable and in order to stabilize them the symmetry needs to be broken: We believe this happens because the gyroid-type TPMS do not exhibit straight lines as graphene does, so there is a competition between the flatness of graphene and the symmetry of the surface. Therefore, when the structure becomes larger, it becomes more graphenic (flat) and the symmetry needs to be broken to be stable, thus producing structures with very low Poisson's ratios close to zero along its faces (see Table 3). From an energetics standpoint, the geometry, and from the average values of the Poisson's ratio, we conclude that the most promising giant Schwarzite to be synthesized is the P-type since it is composed of hexagonal graphene flakes which can be stitched together by a self assembly technique involving edge functionalization. The other cases would require a template such as a mesoporous silicate or an opal type structure [26]. We calculated using DFT, the electronic properties of I-WP Schwarzites, not previously analysed before, finding that they exhibit semiconducting, semimetallic or metallic behavior depending on their size. An interesting point that needs further study is the possibility of finding Dirac cones in giant Schwarzites since these are more graphenic than previously studied cases in which the ratios

of hexagons to octagons is very large.

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