Electronic Structure and Topological Disorder in sp^2 Phases of Carbon

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May 8, 2014

Abstract

Carbon has shown itself to be the most flexible of atoms, crystallizing in divergent phases such as diamond and graphite, and being the constituent of the entire zoo of (locally) graphitic balls, tubes, capsules and possibly negative curvature analogs of fullerenes, the Schwartzites. We compare the various sp^2 -bonded forms of carbon, and describe conditions which open or close the optical gap. We also explore topological disorder in three-coordinated networks including odd-membered rings in amorphous graphene, as seen in some experimental studies. We start with the Wooten-Weaire-Winer models due to Kumar and Thorpe, and then carry out *ab-initio* studies of the topological disorder. The structural, electronic and vibrational characteristics are explored. We show that topological disorder qualitatively changes the electronic structure near the Fermi level. The existence of pentagonal rings also leads to substantial puckering in an accurate density functional simulation. The vibrational modes and spectra have proven to be interesting, and we present evidence that one might detect the presence of amorphous graphene from a vibrational signature.

1 Introduction

Carbon-based semiconductors are one of the hottest topics in condensed matter science. Although silicon-based electronics have achieved tremendous success, scientists and engineers are always seeking alternative materials. One of the main reasons is that the size of silicon-based transistors, which are the building blocks of electronics, is reaching basic limits. One challenge of these short length scales is the requirement of rapid heat dissipation. Nowadays, remarkable improvements in growth techniques allow scientists to build carbon structure with reduced dimensionality in high precision. The advances in computational tools and theoretical models make it possible to investigate and make plausible predictions about the electronic, vibration or optical properties of carbon materials. Single-layer graphene was first isolated by Novoselov et al. using mechanical exfoliation[1]. Graphene's two dimensional structure, which consists only of hexagons, gives rise to its unique and interesting electronic properties and promising potential for applications[2][3]. However, different categories of defects have to be taken into account for applications. It has been shown that these defects may lead to various graphitic arrangements, associated with a menagerie of local minima on the sp^2 carbon energy landscape. Among these analogs of graphite, we will briefly consider the properties of crystalline graphene, fullerene, carbon nanotubes and schwarzite, and focus mainly on amorphous graphene.

2 Computational Methods

To model complex sp^2 carbon systems, the interatomic potential is the fundamental tool to accurately represent the structural electronic and vibrational properties. There are three commonly used interatomic potential in materials theory: empirical potentials, potentials from the tight-binding approximation and *ab-initio* methods[11].

2.1 Empirical Potentials

Empirical potentials are based upon classical chemical concepts. The potential energy function can be expressed as the summation of individual contributions due to various kinds of atomic interactions, which can be categorized into three types[4]: Bonded terms, non-bonded terms and correction terms. By carefully considering different contributions and fitting the experimental data, known properties of the reference materials can be reproduced. Such potentials usually face limits on their ability to represent structures very different from what they were fitted to.

2.2 Tight-binding Approximation

Another commonly used method is the tight-binding scheme. In this approximation, the electrons are considered as tightly bound to the nuclei, and have limited influence on nearby atoms. The single orbital Hamiltonian can be simplified as (following [5]):

$$H = \sum_{\vec{R}} U_{\vec{R}} |\vec{R}\rangle \langle \vec{R}| + \sum_{\vec{R}\vec{R}'} t_{\vec{R}\vec{R}'} |\vec{R}\rangle \langle \vec{R}'| + t_{\vec{R}'\vec{R}} |\vec{R}'\rangle \langle \vec{R}|$$
(1)

Here \vec{R}' represents the nearest neighbors of \vec{R} . The first term in Eq. 1 gives the potential of electron at a lattice site, the second term describes the interaction energy due to hopping between nearest neighbors. For a Bravais lattice, due to symmetry the hopping matrix elements t are same for all lattice sites. For disordered system, they depend on atomic coordinates, which means their values vary from site to site. The free parameters in tight-binding Hamiltonian are obtained by fitting to density functional or experimental results.

The method can make useful predictions about electronic structure, and with appropriate care in the fitting, total energy and forces. Tight binding suffers from transferability issues as Empirical potentials do, though usually less severely, since the tight binding approximation does grapple at least approximately with the electronic structure.

2.3 *ab-initio* Methods

The third well developed set of methods is characterized as *ab-initio*. Since full quantum mechanical calculations are computationally intensive, certain levels of approximations are required for a practical implementation. The dominant approach is density functional theory (DFT). The basic idea used in the density functional setting is to replace the original many-particle wave functions with the ground state charge density as the fundamental variable. This well-accepted theory was introduced by Kohn and Sham (1965). This approximation introduces a set of N single-electron orbitals $|\psi_l(\vec{r})\rangle$, so that the Schrödinger equation (Kohn-Sham equation) can be written as:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_l(\vec{r}) + \left[U(\vec{r}) + \int d\vec{r} \frac{e^2\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\partial\mathcal{E}_{xc}[\rho]}{\partial n}\right]\psi_l(\vec{r}) = \mathcal{E}_l\psi_l(\vec{r}) \tag{2}$$

In Eq. (2) the exchange-correlation $\mathcal{E}_{xc}[\rho]$ due to a superposition of the potential associated with each of the nuclei is still unknown.

Two common approximations have met with widespread use. The simpler approximation is the Local Density Approximation (LDA). This approximation LDA can be expressed as:

$$\mathcal{E}_{xc}[\rho] = \int \epsilon_{xc}[\rho(\vec{r})]\rho d\vec{r}$$
(3)

Here $\epsilon_{xc}[\rho(\vec{r})]$ is the known exchange-correlation energy per particle of the homogeneous electron gas. The exchange energy is given by a simple analytic form $\epsilon_x[\rho] = -\frac{3}{4}(\frac{3\rho}{\pi})^{\frac{1}{3}}[6]$ and the correlation energy has been calculated to great accuracy for the homogeneous electron gas with Monte Carlo methods[7].

The other approximation is the Generalized Gradient Approximation (GGA), which define the functional as[6]:

$$\mathcal{E}_{xc}[\rho] = \int \epsilon_{xc}[\rho(\vec{r}), |\nabla\rho(\vec{r})|]\rho d\vec{r} = \int \epsilon_{xc}[\rho(\vec{r})]F_{xc}[\rho(\vec{r}), |\nabla\rho(\vec{r})|]\rho d\vec{r}$$
(4)

Here $\epsilon_{xc}[\rho(\vec{r})]$ is the exchange-correlation functional of the homogeneous electron gas, and F_{xc} is dimensionless, and based upon three widely used forms of Becke (B88)[8], Perdew and Wang (PW91)[9], and Perdew, Burke and Enzerhof (PBE)[10].

Both empirical potential and tight-binding approximation are computationally cheap relative to *ab-initio*, but suffer from a lack of transferability and reliability in arbitrary bonding environments. *ab-initio* methods are applicable to many systems, but at a significant computational price. Nowadays, SIESTA and Vienna *ab-initio* simulation package (VASP) are two widely used *ab-initio* programs to calculate band structure, electronic density of states, total energies, forces and other quantities. SIESTA uses pseudopotentials and both LDA and GGA functionals[12]. While VASP is based on pseudopotentials, it employs a plane-wave basis and offers various density functionals[13].

3 Crystalline Graphene



Figure 1: The density functional band structure of crystalline graphene. The result of VASP is given by solid line. The results by SIESTA using SZ basis and Harris functional is represented by the dash-dotted curve[17].



Figure 2: Density of states of 800-atom crystalline graphene using both DFT and tightbinding methods. The Fermi energy is 0eV. Solid line represents the result of SIESTA. The density of states due to tight-binding is shown by the dashed line.

Crystalline graphene is just one layer of graphite, in which carbon atoms are arranged on a perfect honeycomb lattice. After experimental isolation in 2004, graphene's electronic properties have been predicted theoretically[31][32][33][34]. Since there have been extensive studies on crystalline graphene, here we will briefly discuss the electronic properties. To calculate the band structure of crystalline graphene, we employed a single- ζ (SZ) basis set with or without Harris functional[14], a double- ζ polarized (DZP) basis set with SIESTA, and also VASP to compute the eight lowest-energy bands. For both SZ and DZP calculations by SIESTA, 20 k-points along each special symmetry lines were taken, and for VASP 50 k-points along each line were sampled. The result from SIESTA using SZ basis and Harris functional is essentially identical with the one based on DZP basis for the four occupied bands. These results of SIESTA with SZ basis and Harris functional and of VASP show excellent agreement with published results for each code respectively[15][16], as shown in Fig. 1. For energies above the Fermi level, agreement of results for the four unoccupied bands are rather poor, which can be amended by carefully choosing the energy cutoff to minimize the total energy as shown by Machon et al.[18]. While this is presumably irrelevant for ground state studies, these artifacts would be significant for transport or optics.

The comparison of density of states of crystalline graphene between DFT using SIESTA and tight-binding methods is shown in Fig. 2. The tight-binding result is calculated based on Eq. (14) in Ref. [2], where t' = 0, t = 2.8eV. Both of these two results around Fermi level can be approximated as $\rho(E) \propto |E|$. The broadening of the DFT DOS is due to incomplete Brillouin Zone sampling.



Figure 3: Optimized structure of C_{240} .

Figure 4: DOS of C_{60} , C_{240} and crystalline graphene. The upper panel shows the whole spectrum, and DOS around Fermi level is given in the lower panel.

4 Fullerenes

In 1985, Kroto et al. found that there exist cage-like molecules containing purely three-fold carbon atoms $(sp^2$ hybridization)[28], which are named fullerenes. This discovery stimulated extensive investigations into this molecular graphite allotrope. Generally speaking, fullerenes refer to a family of closed carbon cages formed by 12 pentagons and various numbers of hexagons, which can be prepared by the vaporization of graphite in an electric arc at low pressure[19]. In this section the electronic properties of C₆₀ and C₂₄₀ will be

discussed. Their structures were optimized by SIESTA with SZ basis and Harris-functional without any symmetry constraints.

The comparison between DOS of these two fullerenes and crystalline graphene are shown in Fig. 4. It appears the curved topology of fullerene opens a gap around the Fermi level. According to Fig. 4 and Table. 1, the HOMO-LOMO gaps of C_{60} and C_{240} decrease with increasing numbers of atoms, which is consistent with other calculations[29]. The evolution of the electronic and phonon density of icosahedral fullerenes as a function of size, and their ultimate convergence to graphene is published elsewhere[20].

5 Carbon Nanotubes

Carbon nanotubes can be visualized as a graphene sheet rolled into a cylinder. There are three different types of carbon nanotubes due to different ways of rolling the graphene sheet. Distinct geometry of these three types give rise to varied electronic behavior. Their structures can be characterized by a chiral vector $\vec{C_h}$ as shown in Fig. 5. Since carbon nanotubes are derived from crystalline graphene, the geometric properties of a carbon nanotube are commonly described by the ones of graphene.



Figure 5: The chiral vector $\vec{C_h}$ shown in honeycomb lattice. \vec{T} is the translation vector, representing the axial direction of the carbon nanotube. Shaded region represents the unit cell of carbon nanotube and Θ is the chiral angle. $\vec{a_1}$ and $\vec{a_2}$ are the lattice vectors of original honeycomb lattice.[21]

Recall that the two unit vectors in the honeycomb lattice are defined as $\vec{a_1} = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right)$ and $\vec{a_2} = \left(\frac{\sqrt{3}a}{2}, -\frac{a}{2}\right)$, where $a \approx 1.42$ Å. To represent the geometry of carbon nanotube according to the original honeycomb lattice, chiral vector $\vec{C_h}$ defines the diameter of carbon nanotube, and translation vector \vec{T} defines the axial direction along the nanotube. Both of them are expressed as:

$$\vec{C_h} = n\vec{a_1} + m\vec{a_2} \vec{T} = \frac{2m+n}{d_r}\vec{a_1} + \frac{-2n+m}{d_r}\vec{a_2}$$
(5)

Here both m and n are integers and n > m. d_r is the highest common divisor of (2n + m, 2m + n). (n, m) values are crucial to the properties of nanotubes. N anotubes with the same number of unit vector indices (n, n) are called armchair nanotubes. Chiral vector indices (n, 0) with m = 0 represents the zigzag nanotubes. Besides these two cases, if the chiral vector indices (n, m) are $n \neq m \neq 0$, the nanotube is called chiral, with a screw symmetry along the axis of the tube[22]. A few examples of these three types of nanotubes are shown in Fig. 6.



Figure 6: Three examples of carbon nanotubes with chiral vector indices (4, 4), (6, 0) and (4, 3) respectively.

To evaluate the electronic properties of carbon nanotubes, we use three carbon nanotubes with different chiral vector indices: (4,4) tube with n = m = 4, (6,0) tube with n = 6, m = 0, and (4,3) tube n = 4, m = 3. Carbon nanotubes exhibit either metallic behavior or semiconductor depending on their chiral indices. Theoretical derivations show that if the indices (n, m) of nanotube satisfy the greatest common divisor of (n-m, 3) is 3, the given carbon nanotube behaves like metal, otherwise, it will be a semiconductor[21]. The Γ point DOS calculation results using SIESTA with SZ basis are shown in Fig. 7. Consistent with the theory, the (6,0) tube has more states around the Fermi level, and obviously is metallic, and (4,3) tube exhibits a gap and is a semiconductor. On the other hand, the (4,4) tube which should be metallic exhibits a gap. In our case, we found SIESTA calculations with SZ basis always tend to overestimate the gap, due to incomplete basis set and Brillouin Zone sampling. By carefully choosing the basis set and fully integraing over the Brillouin Zone, the gap would be reduced. Details of this calculation will be discussed elsewhere.





Figure 7: Normalized DOS of (4,4) tube, (4,3) tube and (6,0) tube. Fermi level is 0 eV. The full spectrums are shown in the higher panel, and lower panel shows in the zooming-in structures around the Fermi level.

Figure 8: Comparison between density of states (DOS) and projected density of states (PDOS) of (30,0) tube and (40,40) tube.

We also compute the Γ point projected density of states (PDOS) using a similar approach for carbon nanotubes. Here we use one zigzag (30,0) tube and one armchair (40,40) tube. According to the law of greatest common divisor of (n - m, 3), (30,0) tube should be metallic, which is consistent with our results as shown in Fig. 8. Also, by comparing the contributions from all three sp^2 orbitals and the p orbital, PDOS on p orbital have significant weight around Fermi energy. And in Fig. 8, the PDOS curves of p orbitals in (30,0) tube and (40,40) tube have identical shape with the DOS around the Fermi level. Thus the electronic properties around the Fermi level is determined by the interaction between p orbitals. This result is in fine agreement with bandstructure calculations, in which the two π bands, which are due to the interaction between p orbitals, determine the metallic behavior of carbon nanotubes[21].

6 Schwartzite

Unlike fullerenes and carbon nanotubes, which have positive Gaussian curvature due to the presence of five-membered rings, schwarzites have negative curvature, which are induced

Allotropes	Models	Gap (eV)	E_{tot}/N_{atom} (eV)
Fullerene	C_{60}	1.724	0.402
	C_{240}	1.231	0.132
Schwarzite	G-384 schw	0.183	0.188
	P-536 schw	0.151	0.112
	P-792 schw	0.086	0.090
	P-984 schw	0.394	0.077

Table 1: The HOMO-LUMO gap and total energy relative to crystalline graphene of various fullerene and schwarzite models.

by seven and eight-membered rings as shown in Fig. 9. As in crystalline graphene, all the atoms of schwarzite are three-fold[23]. To study the electronic properties of schwarzite, four models are used: gycoid 384-atom (G-384 schw), primitive 536-atom (P-536 schw), primitive 792-atom (P-792 schw) and primitive 984-atom (P-984 schw) schwarzite models. DOS of these four models are calculated by SIESTA using SZ basis and Harris-functional with at least $2 \times 2 \times 2$ Monkhorst-Pack grid[24]. The calculation results are given in Fig. 10.





Figure 9: Structure of primitive 792atom schwarzite model. Only half of this model is shown here[25].

Figure 10: Normalized density of states (DOS) of four schwarzite models. Fermi energy is 0eV.

As shown in Fig. 10, with increasing schwarzite unit cell, DOS curve near fermi level approaches to the shape obtained for crystalline graphene as shown in Fig. 2. According to Table 1, increasing the size of the schwarzite cell also leads to decline of HOMO-LUMO gap.

However, the trend breaks at P-984 schw. The total energy per atom also decreases with increasing unit cell size. And the difference in total energy between crystalline graphene and large schwarzite cell approaches 0.077 eV, which suggests there is a real hope to prepare real schwarzite samples.

The calculations of Γ point PDOS of both P-536 and P-792 schw models have been performed. Since the primitive schwarzites contain only 6-member and 7-member rings, and the negative curvature is introduced by 7-member rings, here we compare the PDOS on the atoms within 7-member rings and the ones with 6-member rings, as shown in Fig. 11. It appears that for both of these two models, 7-member rings are responsible for the structure of the DOS around the Fermi level.





Figure 11: PDOS of P-536 and P-792 schw models on 7-member and 6-member rings, and the DOS represent by the dot-dashed lines.

Figure 12: DOS of 800-atom amorphous and crystalline graphene, the Fermi energy is 0 eV[17].

7 Amorphous Graphene

As mentioned in the introduction, crystalline graphene and associated materials have extraordinarily interesting electronic properties. The electronic, thermal, and vibrational properties of graphene depend sensitively on the perfection of the honeycomb lattice. Thus it is worthwhile investigating defects in graphene. Although extensive efforts have been devoted in curved graphene derivatives such as carbon nanotubes and fullerenes, little attention has been given to non-hexagonal defects and their electronic and vibrational properties in a planar graphene. In this section, details about the progress in producing real amorphous graphene samples in experiment, techniques on preparing computational models and calculation results about electronic and vibrational properties of amorphous graphene will be discussed.

7.1 Experimental results

From the 1980's, the progress in the growth engineering and characterization techniques made it possible to grow low dimensional materials under tight control. Recent electron bombardment experiments have been able to create amorphous graphene pieces[26][27]. Clear images of regions of amorphous graphene have been taken by Meyer[30], following the method described in Ref[35].

Recently Kawasumi *et al.* successfully embedded non-hexagonal rings into a crystalline graphene subunit in experiment, synthesized by stepwise chemical methods, isolated, purified and fully characterized the material spectroscopically[36]. They reported the multiple odd-membered-ring defects in this subunit lead to non-planar distortion, as shown in Fig. 2 in [36], which is consistent with our published results, as described in following sections.

7.2 Amorphous Graphene Models

To investigate the electronic and vibrational properties of amorphous graphene, three models are employed: 800 atom model (800 a-g), two 836 atom models (836 a-g1 and 836 a-g2). All these models are prepared by introducing Stone-Wales (SW) defects[37] into perfect honeycomb lattice and a Wooten-Weaire-Winer (WWW) annealing scheme[38] with varying concentration of five, six and seven member rings[17]. Their ring statistics are shown in Table 2. All the atoms in these models are threefold, forming a practical realization of the continuous random network (CRN) model, proposed by Zachariasen[39]. A comparison between crystalline graphene and 836 a-g1 model is shown in Fig. 13.



Figure 13: Top view of 800-atom crystalline and 836-atom amorphous graphene[17].

Ring Size	800 a-g	836 a-g1	836 a-g2
5	33.5	25	24
6	38	53	52
7	24	19	25
8	4.5	3	0

Table 2: Ring statistics of 800 a-g, 836 a-g1 and 836 a-g2 models, shown as %[17].

The electronic DOS of the planar 800 a-g model is compared to a Γ point DOS of the crystalline 800 c-g model in Fig. 12 due to SIESTA. The electronic structure of the 800 a-g model is vastly different from the crystalline graphene near the Fermi level due to the presence of ring defects, as first reported by Kapko et al.[40].

Models	$\delta r({A})$	$\delta ar{r}' \AA$	$E_{tot}/N_{atom}(eV)$
800 a-g	0.01	0.510	-0.086
	0.05	0.526	-0.100
	0.07	0.527	-0.100
836 a-g1	0.01	2.53E-3	0.0
	0.05	1.402	-0.102
	0.07	1.401	-0.102
836 a-g2	0.01	2.72E-3	0.0
	0.05	1.183	-0.090
	0.07	1.180	-0.090

Table 3: The influence of δr on 800 a-g, 836 a-g1 and 836 a-g2 systems relative to the initial flat model[17].

7.3 Symmetry Breaking

The planar symmetry of the original amorphous graphene models is extremely sensitive to external distortions. In the following sections, two different approaches inducing curvature into the original flat graphene models will be discussed.

7.3.1 Random Normal Distortion

Small random distortions have been applied to all the atoms in these three models along the normal direction of the graphene plane. Disordered configurations are relaxed by SIESTA, using SZ basis and Harris-functional. The planar symmetry breaks with curvature above or below the initial plane starting from a flat sheet[17]. The final structures depend on the initial conditions, and share a consistent pattern of relaxation as shown in Table 3.

As shown in Table 3, initially all the atoms have been randomly moved along normal direction by a small displacement $\in [-\delta r, +\delta r]$, as the first column of this table. The

relaxation results are shown in the second and third columns, where the mean displacement of the system away from the original flat plane is given in the second column; and the third column shows the total energy per atom in the relaxed models. Taking 800 a-g model as an example, the electronic density of states (EDOS) around the Fermi level of all the puckered and original flat models are shown in Fig. 14. The influence of puckering on DOS around Fermi level is modest. The puckered system, after relaxation with $\delta r = 0.05 \text{\AA}$ is shown in Fig. 21. Whereas, the mean bond length remains around 1.42\AA , the changes in ring statistics after relaxation are not significant either, as shown in Fig. 15. This implies that it would be difficult to detect puckering using diffraction experiments or the associated radial distribution function.





Figure 14: The EDOS of both flat and relaxed puckered amorphous graphene models. The Fermi level is corrected to 0eV[17].

Figure 15: comparison of RDF of flat and puckered 800 a-g models[17].

To further test the relation between puckering and the initial distortion, various initial conditions have been employed, and puckering structures arise and remain at the same regions[17]. It suggests that rings with certain members may give rise to the puckering. With this motivation, we searched for regions with highest or lowest variations along the normal direction (puckered or smooth regions), as shown in Fig. 16.

As illustrated in Fig. 16, puckered regions tend to have a higher ratio of pentagons to heptagons. The most distorted bonds do not belong to these pentagons, instead they are within the hexagons or heptagons connecting two pentagons. Thus the puckering regions are strongly associated with pentagons.



Figure 16: Enlarged plot of puckered and smooth regions of three amorphous models. Gray atoms are from the puckered configuration, and blue lines represent the original model. (a) The top view of puckered region. (b) The side view of puckered region. (c) The top view of smooth region. (d) The side view of smooth region. [17]

7.3.2 Molecular Dynamics Simulations

Symmetry breaking can also be achieved by Molecular Dynamics (MD) simulations. Calculations are performed with SIESTA with 800 a-g and 836 a-g1 using pseudopotentials and local-density approximations (LDA) with a SZ basis and Harris-Functional at constant volumes. Details about these calculations are discussed in Ref. [41]. It is observed that in every case, even at T = 20K, the system puckers breaking the planar symmetry, reflecting the extremely shallow minimum for the flat structure. In other words, weak thermal disorder is sufficient to induce puckering. The relation between total energy of the system and the maximum separation of atoms along the normal direction (magnitude of puckering) is shown in Fig. 17. It indicates loosing planar symmetry will lower the total energy of the system, which is consistent with our results due to random distortions as shown in Table 3.

7.4 Conformational Fluctuation

As mentioned in the previous section, several constant temperature MD simulations have been performed. The main purpose of this section is to investigate the nature of puckering minima of amorphous graphene, which can be induced by different initial conditions as we observed before [17] and is also a universal phenomina in amorphous materials [42]. Here we employ the method proposed by Fedders and Drabold [42], which is akin to the conformational space annealing approach mentioned in Ref. [43]. Starting with a perfectly relaxed model (in our case 800 a-g and 836 a-g1), during each MD simulation we let the network evolve for 8.0 ps at four different mean temperatures of 20, 500, 600, or 900K





Figure 17: Correlation between the total energy per atom and magnitude of puckering for constant temperature MD simulations. Zero total energy refers to the total energy of original flat 800 a-g model.[41]

Figure 18: Time variation of two autocorrelation functions. This figure shows autocorrelation functions of $\Delta \theta(t_1, t_2)$ and $100\Delta r(t_1, t_2)$ with $t_1 = 6.0ps$ and t_2 varying from 6.0 to 7.95 ps.[41]

using Berendsen thermostat (velocity rescaling) to achieve the target temperatures. Then snapshots have been taken every 0.15 ps and quenched to find the metastable minima (or unique basins on potential energy landscape (PEL)[43]).

To investigate the conformational changes between these quenched minima, two auto correlation functions are used as defined as Fedders and Drabold[42]:

$$\Delta\theta(t_1, t_2) = \sum_{i} ((\theta_i(t_1) - \theta_i(t_2))^2 / N)^{\frac{1}{2}}$$
(6)

$$\Delta r(t_1, t_2) = \sum_i ((r_i(t_1) - r_i(t_2))^2 / N)^{\frac{1}{2}}$$
(7)

Where θ_i is the i^{th} bond angle, and r_i represents the distance between i^{th} nearestneighbor pair. Time t_1 and t_2 refer to two distinct quenched snapshots. These autocorrelation functions provide an insight into how thermal MD simulations lead to transition between various energy basins. Taking 800 a-g model as example, its autocorrelation functions are shown in Fig. 18. It appears $\Delta \theta(t_1, t_2)$ and $\Delta r(t_1, t_2)$ from MD runs at three different temperatures are qualitatively similar. They all increase linearly initially and fluctuate about a constant eventually. The continuity of these curves suggests there exists a continuum of states, which differ structurally in moderate ways. The results using 836 a-g1 have great consistency with 800 a-g.

The total energy distributions of all these quenched snapshots from MD runs at different temperature are shown in Fig. 19. Excepting quenched configurations from 20K MD,





Figure 19: Total energy distribution functions of quenched supercells from MD runs under 20, 500, 600, and 900 K. The total energy of original flat 800 a-g is considered as 0 eV.[41]

Figure 20: VDOS of 800 crystalline graphene, pucker-up and -down a-g models.[41]

the total energy distributions exhibit several peaks. The annealing process at the beginning of each MD simulation is responsible for the minor peaks on the right side of Fig. 19. The major peaks (labeled as 3, 2, 1 in Fig. 19) are contributed by the distinct puckering supercells sampled while MD simulations achieving equilibrium at constant T. Correspondingly in Fig. 18, autocorrelation functions reach an asymptotic state after around 7.0 ps. Thus each of these three peaks in Fig. 19 demonstrates a basin on the PEL of amorphous graphene. A series of nearly degenerate quenched minima are trapped in distinct basins on the PEL, forming a continuum metastable state around inherent structures. Details of the topological variations are discussed in Ref. [41]. The average total energy variation between these basins corresponding to the three major peaks in Fig. 19 is around 1.405×10^{-3} eV, and these quenched configurations belonged to distinct basins share identical local bonding. The only difference is that they pucker in unique ways. Parallel calculations of 836 a-g1 reveal close agreement with the results of 800 a-g as stated above.

Analogous calculations using a 64-atom model of a-Si reveal that PEL of 3D system (a-Si) is smooth consisting of one general basin[41]. By investigating the correlation between topology and energy level of these quenched minima, it appears that lower total energy (more stable state) corresponds with more puckered (higher surface roughness) configurations with minute variation in bond lengths and angles from the original flat 800 a-g model.

7.5 Phonon Calculation

To study vibrational properties of amorphous graphene, calculations of the dynamical matrix, eigenvalues and eigenvectors are performed for the original flat 800 a-g and 836 a-g1 models, and their puckered derivatives. The dynamical matrix was constructed from finite difference calculations (using six orthogonal displacements of 0.04 Bohr for each atom). Phonon calculation has also been performed for an 800-atom crystalline graphene model (800 c-g). Though there exist certain topological difference between 800 a-g and 836 a-g1, their vibrational properties are consistent with each other, as well as their puckered derivatives. In what follows, we'll emphasize on the results of 800 a-g model.

For the puckered configurations of 800 a-g model, we focus on two quenched configurations with certain regions puckering in opposite directions, designated "pucker-up" and "pucker-down" models, as shown in Fig. 21.



Figure 21: Side view of pucker-up and -down 800 a-g models. Gray balls and sticks illustrate pucker-up model, and pucker-down supercell is represented by blue lines.[41]

7.5.1 Vibrational density of states

The vibrational density of states (VDOS) of 800 c-g model, pucker-up and pucker-down 800 a-g models are shown in Fig. 20. The VDOS of crystalline graphene shows great agreement with a published result[44]. In Fig. 20, the spectrum of crystalline graphene reach a minimum at a frequency near $1375cm^{-1}$, whereas the spectrum of two puckered amorphous configurations achieve a local maximum. Thus Raman scattering experiments could provide a way to distinguish crystalline and amorphous phases of graphene. While dealing with a mixed sample containing 3D amorphous carbon, this alternation from ordered graphene near $1375cm^{-1}$ might not be very helpful, since in various phases of a-C (with varying sp²/sp³ ratio) many modes have been observed near the relevant energy[45][46][47]. Between pucker-up and -down 800 a-g models there is no significant difference in the spectrum.

7.5.2 Vibrational modes

In both the original flat 800 a-g and 836 a-g1 models, there exist eigenvectors with imaginary eigenvalues, whose components along the normal direction of the graphene plane is much larger than the other ones (at least four orders of magnitude higher than longitudinal ones). Two examples of these imaginary-frequency modes are given in Fig. 22. It appears these modes are localized on pentagons in the configurations. According to previous discussion in Sec. 7.3.1, pentagons are the origin of puckering and symmetry breaking. Thus these imaginary-frequency modes give us clean evidence about the pentagon-induced instability of the flat amorphous graphene models.



(a) Imaginary-frequency mode in flat 800 α -g model with frequency $\omega = 283.843 i cm^{-1}$ (referred as im-model).



(c) Side view of the region where im-model is originally localized.



(b) Imaginary-frequency mode in flat 800 α -g model with frequency $\omega = 272.661 i cm^{-1}$ (referred as im-mode2).



(d) Side view of the region where im-mode2 is originally localized.

Figure 22: Two examples of imaginary-frequency modes in flat 800 α -g model. The contour plot represents the component of eigenvector along the direction transverse to the plane.[41]

In the puckered models, modes with very low frequency, around $14-20 \text{ cm}^{-1}$, have been observed. These modes remind us of "floppy modes" proposed by Phillips and Thorpe[48][49]. These low-frequency modes are rather extended, and have compelling weight on pentagonal puckering regions and large rings, as shown in Fig. 23. This is consistent with the results obtained by Fedders and Drabold in a-Si:H[42]. The lowest-frequency acoustic phonon modes in an identical sized crystalline graphene model are almost twice larger than the energy scale of these low-frequency modes in amorphous graphene, which is around a few meV. As pointed out by the theory of "two-level systems", there exists a distribution of low-energy excitations, caused by tunneling of atoms between nearly degenerate equilibrium states[50][51]. As mentioned in Sec. 7.4, the energy variations between minima within one basin is in the order of 10^{-4} eV, and the energy difference between basins is in the order of 10^{-3} eV[41]. Then then energy of these low-frequency modes (meV) is sufficient to cause conformational variations around one minima (within one basin), but not high enough to overcome the barrier between different basins on PEL.



(a) Low-frequency mode in pucker-down 800 α -g (b) Low frequency mode in pucker-up 800 α -g model model with frequency $\omega = 19.167 cm^{-1}$. with frequency $\omega = 17.318 cm^{-1}$.

Figure 23: Examples of low-frequency modes in pucker-down and -up 800 α -g models. The contour plots represent the intensity of eigenvectors on each atom. The blue atoms illustrate the "puckering-most" atoms, and the green atoms represent "flat" atoms.[41]

In the high-frequency range, we observe some highly-localized high-frequency modes, which is due to pentagonal defects[41]. This is consistent with the observation of Biswas et al.[52] and Fedders et al.[53], who have concluded strain and topological defects are active at high frequencies.

8 Conclusion

In summary, positive curvature opens up a HOMO-LUMO gap in fullerenes. For carbon nanotubes, their electronic properties strongly depend on the chiral indices. On the other hand, the influence of negative curvature on DOS is reduced by increasing schwarzite unit cell size, and the difference of DOS between large schwarzite and crystalline graphene diminishes. For both positively and negatively curved carbon allotropes, the bigger the closed cage is, the lower the total energy per atom will be.

For amorphous graphene, presence of pentagons and heptagons induces extensive states around Fermi level, and pentagons increase the sensitivity of whole system to external distortions leading to puckered states. A series of MD and quenching simulations suggest these puckered states correspond to distinct local minima on PEL of amorphous graphene, whose boundaries can be overcomed by heating up the system. Each basin on PEL is associated with a continuum of bond length, bond angles and energy scale, which is consistent with the studies of α -Si:H in 1996[54].

Vibrational calculations reveal the existence of localized imaginary-frequency modes in flat 800 a-g model, which are localized on pentagons and play the key role in breaking planar symmetry. Delocalized low-frequency phonon modes, akin to floppy mode, have substantial weight on pentagonal puckering regions and are triggered by the transition between adjacent basins on the PEL.

Acknowledgements

Here we want to acknowledge Dr. M. F. Thorpe at Arizona State University and his group members, who have prepared all the amorphous graphene models, Dr. Mingliang Zhang and Dr. Binay Prasai for their suggestions, and Dr. Humberto Terrones at Penn State University for his kindly help. The calculations of radial distribution function are done by ISAACS[55]. This work is supported by the Army Research Office.

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