Negatively Curved Graphitic Sheet Model of Amorphous Carbon

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A computational method has been developed for generating graphitic carbon structures on an arbitrary smooth surface and with a given number of carbon rings. Using both periodic and random surfaces for constraint, many extended graphitic carbon structures have been generated. The energy relative to graphite and the bulk elastic properties have been calculated. Like their periodic counterparts, the random structures are found to be exceptionally stable. Their radial distribution functions match closely those of films of amorphous carbon grown on NaCl substrates from sublimated graphite.

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The recent discovery of a method to produce fullerenes in bulk [1] and the observation of graphite tubules [2] have prompted speculation about new, related forms of carbon. Recent proposals involve graphitic sheets with negative Gaussian curvature [3–5]. This form of carbon has been called schwarzite, after the mathematician H. A. Schwarz who first studied the periodic minimal surfaces these structures resemble [6]. Calculations have shown that some schwarzite structures are much more stable than C_{60} [3,5,7,8].

Although crystalline schwarzites could be strong and lightweight materials [5], it has been noted that random pore geometries are more likely to be formed [3,5]. To facilitate the study of these forms of carbon we have developed a method for automatically generating graphitic carbon structures constrained to an arbitrary smooth surface and containing any number of carbon rings. A similar method was developed independently [9] for the study of fullerenes and has recently been applied to *P*-type crystalline schwarzite [7].

Several distinct forms of hydrogen-free amorphous carbon are known experimentally [10–12]. The most common form of amorphous carbon is sp^2 rich [13], although the ratio of sp^2 to sp^3 bonding can be varied under appropriate conditions [10]. A form known as glassy carbon can be produced by pyrolysis. It can be thought of as tangled ribbons of graphite, containing curved sheets of almost entirely six-membered rings [14]. These curved sheets are stacked with a spacing similar to that found in graphite, an arrangement known as turbostratic. Other sp^2-rich forms of amorphous carbon have been produced by magnetron sputtering and thermal sublimation of graphite. These lack crystalline ordering within the sheets [13] as well as having a considerably weakened (0002) diffraction peak characteristic of the graphite intersheet spacing [12]. Neutron [13] and electron [12] diffraction studies agree best with structural models containing significant fractions of non-six-membered rings, though these models only agree up to the length scale of one ring.

The graphitelike sheets we consider can be curved into spheres, cylinders, minimal surfaces, or even random surfaces. Thus our algorithm requires the specification of an arbitrary smooth surface defined by the equation $f(\mathbf{x})=0$, where $\mathbf{x}$ denotes position in space. The *D*, *P*, and *G* minimal surfaces [15] are approximately represented by periodic functions constructed from low-order Fourier modes. For example, we used the function

$$f(\mathbf{x})=\cos(2\pi x_1)+\cos(2\pi x_2)+\cos(2\pi x_3) \tag{1}$$

for the *P* surface. For the random surfaces we used the boundary between domains in a three-dimensional fcc Ising model quenched from high temperature with spin-conserving Monte Carlo dynamics. Neglecting the anisotropy due to the underlying fcc lattice, the Ising energy of the interdomain surface is proportional to its area. The Monte Carlo procedure lowers this energy and thus the area as it proceeds. The function $f(\mathbf{x})$ is obtained from a fast Fourier transform of an array that is -1 for down spins and $+1$ for up spins. The series is truncated to remove roughness due to the 32^3-point lattice. This procedure produces a single sheet dividing the cell into two nearly equal volumes.

Our method for covering these surfaces with carbon networks was motivated by considering graphite monolayers, in which ring centers form a regular triangular array. We generate a candidate structure by forming a triangular array of points with necessary disclinations on an arbitrary smooth surface. Initially, a number of points equal to the desired number of rings are placed randomly on the surface. A cost function is taken to be a purely repulsive pair potential summed over pairs and is minimized using simulated annealing. An individual step consists of moving a single point randomly on the surface. On completion, the points define the centers of the rings. The carbon structure is extracted by triangulating these points, placing carbons at the centers of the triangles, and bonding the carbons in adjacent triangles. Finally, the structure and its unit cell size are relaxed to a minimum of the energy estimate of Ref. [5]. This energy estimate was shown to be accurate to within 0.04 eV/atom for crystalline schwarzite [7,8]. Elastic moduli are computed from the energetics of small distortions.

Many possibilities were examined for carbon structures on the periodic minimal surfaces *D*, *P*, and *G* [15]. Structures with high symmetry within the cell were found with 200 and 216 carbons on the *D* surface; 56, 168, and 216 carbons on the *P* surface; and 56 and 216 carbons on

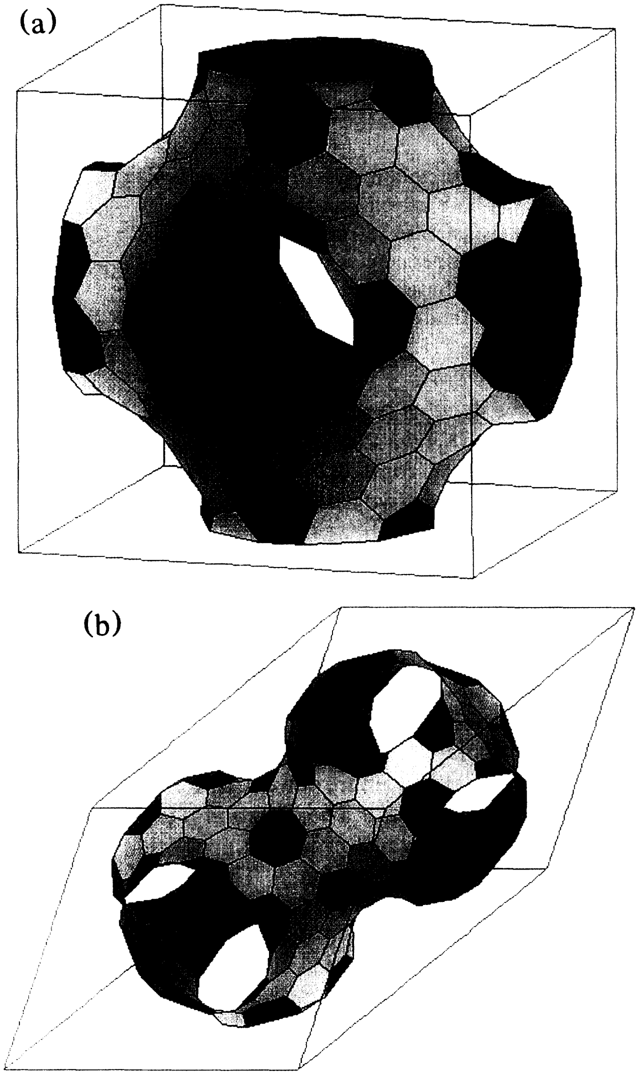

FIG. 1. Views of two new crystalline schwarzites. Each has 216 carbon atoms per primitive unit cell with 80 six-membered rings (blue) and 24 seven-membered rings (orange). The structure in (a) lies on a P minimal surface in a cubic cell 15.7 Å on a side. The structure in (b) lies on a D minimal surface in an fcc cell whose cubic lattice constant is 24.6 Å.

the G surface. Many combinations of numbers and surfaces seemed to favor disordered structures (often containing five-membered rings). Even when lower in cost function, symmetric structures were computationally costly to generate. Symmetric structures were found with 216 atoms on each of the three minimal surfaces. We attribute this to the favorable divisibility of 216 with respect to the symmetries of these surfaces. Among the high-symmetry structures seven-membered rings were sometimes all paired [Fig. 1(a); row 1, Table I], sometimes all isolated [Fig. 1(b); row 2, Table I], and sometimes both paired and isolated. Thus adjacent seven-membered rings are feasible in these structures, unlike adjacent five-membered rings in fullerences.

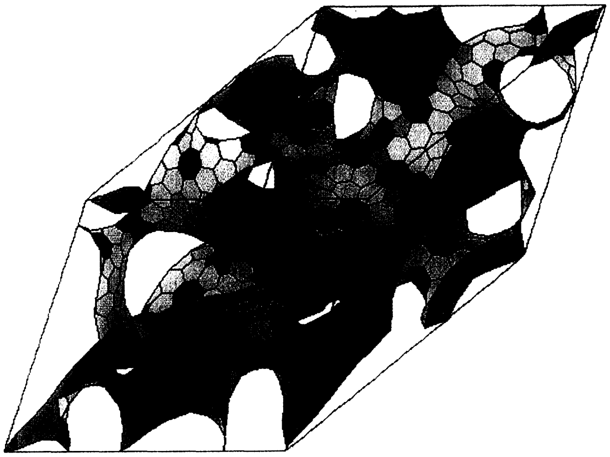

FIG. 2. View of a random schwarzite model on a surface of genus 12 per fcc supercell. The structure has 1248 carbons arranged into 38 five-membered rings (yellow), 394 six-membered rings (blue), 155 seven-membered rings (orange), 12 eight-membered rings (green), and 1 nine-sided ring (pink). Slower annealing produces a structure with many fewer five-membered rings. The cubic unit cell (4 times the volume of the fcc cell shown) is 42.9 Å on a side.

A random surface having genus 12 per supercell (Fig. 2) was used to generate a series of structures. Three different numbers of carbons (848, 1248, and 1648) were tried, each with three different ring annealing schedules. Four runs, each on a different random surface created with the same Ising-model parameters, showed sizable variation in bulk modulus (36% range) but little variation in stability (8% range) and radial distribution function. As shown in Table I, the random structures are similar in stability to crystalline schwarzites. Though the random structures contain isolated regions of high curvature, the overall energy estimate is still reliable due to the small extent of these regions. The cubic shear modulus C_{44} of the random schwarzites is similar to that of the crystalline schwarzites. Shear in both sorts of structures mainly involves sheet bending rather than bond compression. In contrast, the bulk modulus of the random structure is reduced; compression is obtained mainly through sheet bending with little bond compression, due to the random geometry.

It is interesting to compare the random schwarzite models with amorphous carbon (a-C) films having nearly 100% sp^2 bonding. Films were grown under a vacuum of 10^{-6} Torr by electron beam heating of a graphite target, producing an almost pure sp^2 form of carbon commonly known as thermally evaporated amorphous carbon. The films were prepared by a NaCl substrate heated to 300 °C and floated onto electron microscope grids in distilled water. Energy-filtered electron diffraction patterns were obtained at the Sydney University electron microscope unit with a Phillips EM430 transmission electron microscope fitted with a GATAN parallel electron energy loss spectrometer [18]. Care was taken to work only with

TABLE I. Bulk properties of various forms of carbon. Density is denoted by ρ, energy per atom relative to a graphite monolayer by ΔE, bulk modulus by B, and cubic shear modulus by C_{44}. The first three rows are for structures shown in Figs. 1 and 2. All rows except the last two are for theoretical structures whose properties have been calculated using the energy estimate of Ref. [5].

Structure	ρ (g cm^{-3})	ΔE (eV)	B (Mbar)	C_{44} (Mbar)
Schwarzite P216 [Fig. 1(a)]	1.11	0.17	1.01	0.19
Schwarzite D216 [Fig. 1(b)]	1.16	0.16	1.07	0.16
Schwarzite 1248 (Fig. 2)	1.26	0.23	0.49	0.14
Schwarzite G216	1.18	0.17	1.09	0.18
Schwarzite P216 (Ref. [5])	1.02	0.20	0.75	0.15
Schwarzite P192 (Ref. [4])	1.16	0.19	1.03	0.17
Schwarzite D216 (Ref. [5])	1.15	0.18	0.94	0.16
Schwarzite D168 (Ref. [3])	1.28	0.22	1.15	0.20
fcc C_{60} (Refs. [16,17])	1.71	0.42	0.14	···
Diamond	3.52	0.02	4.43	5.76

films thinner than 200 Å and a beam voltage of 300 keV so that multiple scattering was negligible. Fourier sine transformation of the reduced diffraction intensity $\phi(s)=s[I(s)/Nf^2(s)-1]$ yields the reduced density function $G(r)=4\pi r[\rho(r)-\rho_{\text{ave}}]$, as discussed in earlier papers [19]. Here $I(s)$ is the energy-filtered diffraction intensity, $f(s)$ the atomic scattering factor, $\rho(r)$ the average density of distance r from an atom center, and ρ_{ave} the density averaged over the complete specimen. The scattering vector $s=2\sin\theta/\lambda$ was sampled out to $s_{\max}=3.5$ Å^{-1}.

The a-C film was found to have an average bond length of 1.422 ± 0.008 Å and an average bond angle of 119.8 ± 0.1 deg. From the energy loss spectrum the plasmon peak energy was found to be 23 eV. The bulk density then estimated from the free electron relationship was 1.9 g/cm^3. This figure places an upper bound on the bulk density since no signal will be obtained from regions containing voids larger than a characteristic plasmon wavelength of about 5 Å [20]. For instance, the measured plasmon peak of 25 eV in a C_{60} thin film would suggest a density of 2.2 g/cm^3 compared to the true density 1.71 g/cm^3. A similar a-C with a density of 2.0 g/cm^3 as determined by flotation methods has a plasmon energy of 24 ± 0.5 eV which would imply a density of 2.1 ± 0.1 g/cm^3 [12].

As shown in Fig. 3, the agreement between the $G(r)$ for the a-C film and the random schwarzite is quite good. The $G(r)$ for the model structure was calculated using the Debye formula:

$$\phi(s)=\frac{2s}{N}\sum_{m=2}^{N}\sum_{n<m}^{N}\frac{\sin 2\pi s r_{mn}}{2\pi s r_{mn}}, \tag{2}$$

where r_{mn} is the distance between atoms m and n. The $\phi(s)$ was computed for the same range of s as in the experimental data and processed in the same manner as the experimental data. This introduces the same instrumental broadening into the theoretical $G(r)$ as is present in the experimental one. The agreement between theory and experiment for the first and second peaks is to be expected due to the similar bond lengths, bond angles, and coordination numbers in the two structures. The region between the second and third peaks contains distances characteristic of five-, six-, seven-, and eight-membered rings, while the region of the third peak contains distances between adjacent rings. Agreement beyond this point indicates similarities in sheet curvature. The random model with 1248 carbons was found to fit best in this long-range regime. One discrepancy between theory and experiment is the somewhat lower density of the random schwarzite. While $G(r)$ is not very sensitive to differences in density, the different slopes at small angles in $I(s)$ (Fig. 4) suggest that the two materials have different macroscopic densities. The random schwarzite is a very porous structure, with no instances of parallel stacked sheets. One possibility is that the a-C is very similar in structure but contains sufficient regions of doubled sheets to increase the density. Since the dominant contribution would still be from in-plane distances, the overall shape of $G(r)$ would not be substantially changed. This cannot be ruled out by our experiments.

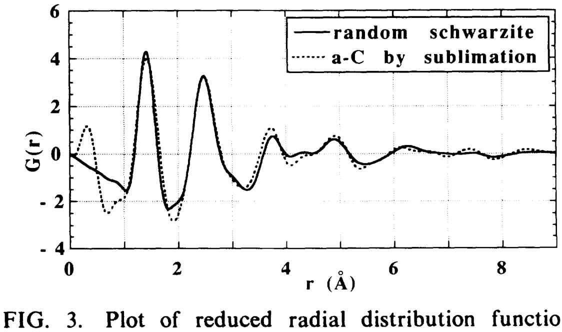

FIG. 3. Plot of reduced radial distribution function for thermally evaporated amorphous carbon and the same data computed for the random schwarzite shown in Fig. 2. The oscillation in the experimental curve below 1 Å is an artifact.

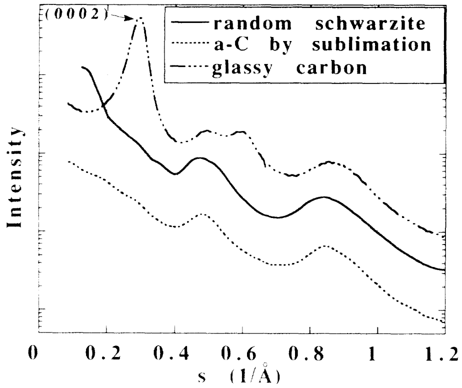

FIG. 4. Diffracted electron intensity vs $s=(2\sin\theta)/\lambda$ for thermally evaporated amorphous carbon, glassy amorphous carbon, and the random schwarzite shown in Fig. 2, where θ is the scattering angle measured from the beam direction and λ is the wavelength. The intensity is plotted on a logarithmic scale making the vertical placement of the curves arbitrary. The curves are shown separated for clarity.

A comparison of the small-angle region of the calculated and experimental diffraction patterns, Fig. 4, shows a wide range of small-angle scattering corresponding to large-scale structure. The (0002) reflection corresponding to the 3.3-Å interlayer distance in graphite is very weak for our *a*-C. This suggests that if there is double sheeting in the actual structure at all, the registration between sheets is poor, as one would expect for highly curved sheets with many non-six-membered rings. For comparison, the diffraction pattern of a glassy carbon is shown. This has a very pronounced (0002) reflection as expected for its turbostratic structure [14].

The stability of our random models suggests that a mechanism capable of producing crystalline order might not be necessary for the formation of schwarzite. The seeming abundance of stable structures among the possible arrangements of carbon in sheets adds to the plausibility of the formation of such solids. Moreover, the close match between the reduced radial distribution function of amorphous carbon grown by sublimation and our random schwarzites may indicate that random schwarzite-like materials have already been produced. Perhaps some related set of experimental conditions could produce more ordered versions of these materials.

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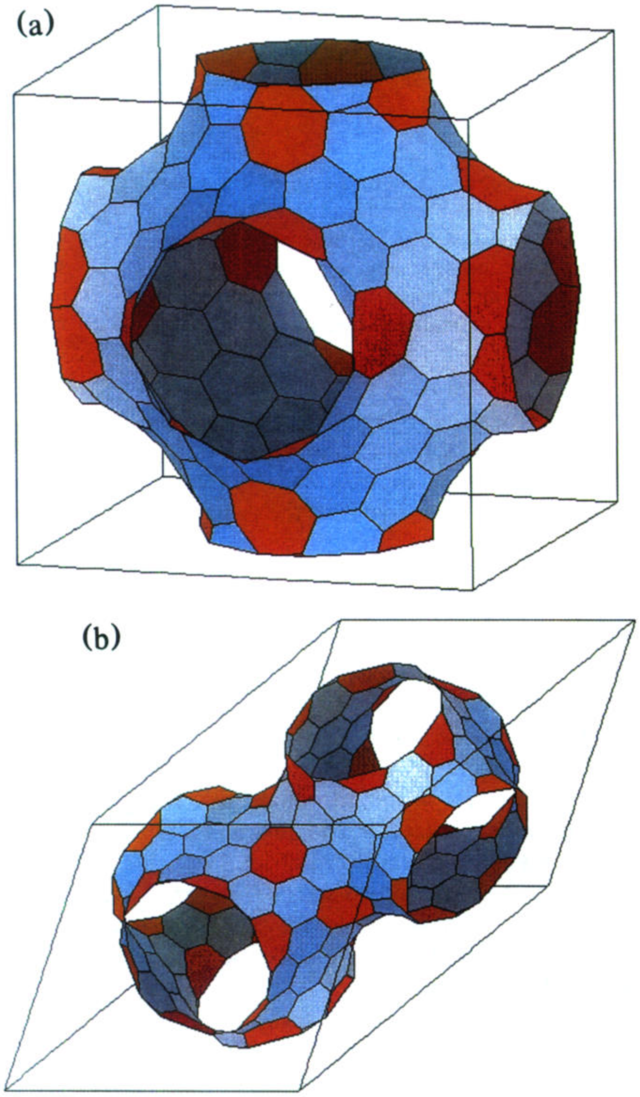

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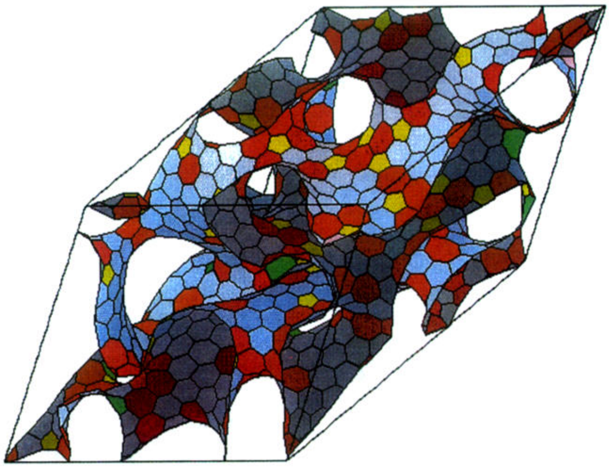

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