PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1996 **354**, 1999-2008
doi: 10.1098/rsta.1996.0088

Elastic warping of graphitic carbon sheets: relative energies of some fullerenes, schwarzites and buckytubes

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The energies of hypothetical and the already found 'graphitic' (sp^2) carbon networks with hyperbolic ('schwarzites'), elliptic ('fullerenes') and parabolic ('buckytubes') curvatures are compared with a simple elastic model of the warping energy of a spontaneously flat graphite sheet, analogous to bending energy models for amphiphilic membranes, invoking both bend and twist contributions. Splay and saddle splay moduli are estimated to be $190kT$ and $-65kT$, respectively, an order of magnitude stiffer than typical amphiphilic bilayer membranes. The model accounts adequately for relative self-energies of most curved graphitic networks. Many proposed allotropes of carbon may thus be treated as two dimensional warped layer-structures.

1. Introduction

The discovery of fullerenes (Kroto *et al.* 1985) initiated a storm of scientific activity in all aspects of carbon physics and chemistry. The dust has now settled, and it is timely to reflect on the changed scientific landscape brought about by this discovery.

At the fundamental level of condensed atomic matter modelling, fullerenes are a challenge to our usual notions of atomic structure. First, they demonstrate that colloidal dimensions and mesoscopic length scales (of the order of 50 Å), commonly seen in liquid crystalline molecular assemblies, can be found in simple atomic systems. This conclusion has since been amply confirmed by studies of mesostructured aluminosilicates of the MCM family, first announced by Mobil researchers (Kresge *et al.* 1992), as well as other inorganic materials (Huo *et al.* 1994). Second, the understanding of fullerene and associated carbon structures requires the tools of surface geometry: differential geometry and topology. In other words, warped non-graphitic sp^2 carbon polymers can be formally viewed as two-dimensional non-Euclidean structures, i.e. curved surfaces.

The latter claim is particularly thought provoking, since the notion of dimensionality of condensed atomic structure has until now been innocuous: graphite is a classic example of a layer-structure, and is two dimensional, while the framework of diamond, the sp^3 carbon polymer, is three dimensional. This traditional classification does, however, invoke the unspoken assumption that one is better off adopting a Euclidean rather than a non-Euclidean description. We shall adopt the opposite

Phil. Trans. R. Soc. Lond. A (1996) **354**, 1999–2008
Printed in Great Britain

TEX Paper

assumption: that fullerenes, graphite and the (as yet undiscovered) schwarzite frameworks are all examples of warped layer-structures and discuss its consequences. The analysis leads to the surprising conclusion that only the densest proposed hyperbolic polymeric forms of sp^2 carbon deserve to be labelled as three dimensional.

The first, less contentious, claim, that these exotic allotropes of carbon exhibit characteristic lengths similar to those found in liquid crystals, led us to investigate the possibility that the simple theory of bending energy of amphiphilic films in lyotropic liquid crystalline mesophases could be applied to fullerenes and schwarzites. Indeed, the mesostructural correspondence between fullerenes and spherical micelles, buckytubes and rod-shaped micelles, graphite and lamellar phases, and schwarzites and bicontinuous cubic phases is striking. It is likely that this correspondence lies at the heart of the synthetic route to mesostructured inorganic materials with frameworks templated by lyotropic liquid crystals (Huo *et al.* 1994).

We first outline a simple phenomenological theory of the energy required to warp atomic networks, akin to the stability theory of self-assembled molecular membranes. This is then compared with self-energy data available for a range of fullerenes and schwarzites, and two rigidity moduli, the bend and twist moduli, for sp^2 carbon films are deduced. Finally, the usefulness of this two-dimensional view of these materials is discussed.

2. Warping energy

Conventional stability theory for amphiphilic molecular membranes is built around the assumption that the interface(s) between immiscible molecular moieties have a 'preferred curvature', and deviations from that 'relaxed' curvature state—whether by splay or saddle splay deformations—incur a bending energy (enthalpic) cost. In an elegant analysis, Helfrich (1973) demonstrated that the functional form for the bending energy of a membrane, the spontaneous (mean) curvature of which is H_0, is, within the elastic approximation,

$$E_{\text{bend}} = \kappa(H - H_0)^2 + \overline{\kappa}(K), \tag{2.1}$$

where H and K denote the mean and Gaussian curvatures, respectively, and κ and $\overline{\kappa}$ are the splay and saddle splay elastic moduli for the membrane. These curvatures are related to the principal curvatures of the surface, k_1 and k_2 by the relations

$$H = \tfrac{1}{2}(k_1 + k_2), \quad K = k_1 k_2. \tag{2.2}$$

Complications notwithstanding, this simple formula (2.1) throws much light on the complex issue of amphiphilic molecular self-assembly (Fogden *et al.* 1991). Experimental measurements suggest that the splay bending modulus lies between 1 and $10kT$ for typical amphiphilic assemblies; the saddle splay modulus $\overline{\kappa}$ is smaller in magnitude than κ, and may attain either sign (Lipowsky 1991).

This phenomenological approach to curved structures is applicable to a range of elastic materials, provided that they can be modelled by a very thin film (thin compared, for example, with a typical radius of curvature of the film), and provided that interactions within the material are short-range and act along the film. It is known from graph theory that any network can be embedded in at least one orientable surface; this is ensured by 'König's theorem' (Lindsay 1959). It is therefore feasible to extend this formalism to atomic networks, although such an approach may well apply only to low-density frameworks, in the limit of very small distortions of the framework about some 'preferred' reference state. This preferred state is one for which all bond lengths and angles match those expected to be most favourable, e.g. tetrahedral bonds for sp^3-bonded frameworks. Although it may seem unlikely that elastic models can capture the complexities of interatomic bonding energetics, several reports have suggested that the sp^2 carbon bonding networks can be reasonably well modelled using simple quasi-elastic functional forms which account for the energetic cost involved in bending deviations from planarity of the bonding network (Schmalz *et al.* 1988; Adams *et al.* 1992). Within the tight-binding approximation the energy associated with bending the network from a plane by an angle ϕ can be approximated by the functional form

$$E_{\text{bend}} = \kappa_{\text{bend}}(1 - \cos(\phi)). \tag{2.3}$$

Warping of the planar graphitic network is required to form closed-shell fullerenes or open hyperbolic schwarzites. This warping is accompanied by two distinct deformation modes of the carbon network: bend (*curvature*) and twist (*torsion*). These deformations can be calculated using the following construction. Rings in the network are first 'filled in' to give a surface, the surface density of vertices of which is as large as possible. This construction is trivial for (quasi-spherical) fullerenes; for schwarzites it is more subtle (Hyde 1993*a*). A unique 'director vector' (the surface normal) is associated with each point along an edge of the network. If the network is non-planar, the director changes orientation from one vertex to another. The component of this change in the local plane containing the director and the tangent vector to the edge is the bend deviation, ϕ. The change in the plane normal to the edge containing the director is the local twist angle, θ. In the language of differential geometry, the bend angle is the *normal curvature*, and the twist is the *geodesic torsion*. By analogy with (2.1) and (2.2), we can ascribe a warping energy cost for deformation from the graphitic network:

$$E_{\text{warp}} = \kappa_{\text{bend}}(1 - \cos(\phi)) + \kappa_{\text{twist}}(1 - \cos(\theta)). \tag{2.4}$$

If the edges are all of length l, the bend and twist deformations per vertex for the ith edge emanating from that vertex can be replaced by curvature, k_i, and torsion, τ_i, integrated from the vertex up to the mid-point of the edge:

$$\phi_i = \int_0^{l/2} k_i \, \mathrm{d}s, \quad \theta_i = \int_0^{l/2} \tau_i \, \mathrm{d}s. \tag{2.5}$$

These angles depend on the Gaussian and mean curvatures of the surface containing the network, as well as the tangential directions the edges adopt with respect to the orthogonal principal directions on the surface. The network curvature and torsion are related to the principal curvatures k_1 and k_2 of the surface by the equations

$$k_i = k_1 \sin^2 \omega_i + k_2 \cos^2 \omega_i \tag{2.6}$$

and

$$\tau_i = (k_1 - k_2) \sin \omega_i \cos \omega_i, \tag{2.7}$$

where ω_i is the angle between a principal direction at a point P on the surface and the ith edge direction passing through P. These equations expose the complementary nature of curvature and torsion, or bend and twist. For a non-spherical surface, edges lying along the principal directions are torsion-free, yet maximally bent. In contrast to that case, the 'flattest' net on a given surface is one with edges that lie along the asymptotic directions of the surface; this net is maximally twisted.

Imagine laying down a three-connected network, such as a sp^2 carbon net, on a surface of arbitrary curvature. Assume that the edge directions at the vertices subtend angles of $\frac{2}{3}\pi$ with each other, so that

$$\omega_i = \omega + \tfrac{2}{3}\pi i. \tag{2.8}$$

Assume further that the curvatures of the surface are constant across the surface, so that the integrals in (2.5) reduce to simple products. For small values of the curvature and torsion, both scaled by the length l, (2.4) adopts the form

$$E_{\text{warp}} \approx \sum_{i=1}^{3} [\kappa_{\text{bend}}(\tfrac{1}{8}k_i^2 \cdots) + \kappa_{\text{twist}}(\tfrac{1}{8}\tau_i^2 \cdots)]. \tag{2.9}$$

Expanding (2.9) to quadratic order, using (2.6) and (2.8), leads to an expression for the warping energy per vertex in terms of the principal curvatures of the surface:

$$E_{\text{warp}} \approx \tfrac{3}{64}\{\kappa_{\text{bend}}[3(k_1 - k_2)^2 + 8k_1k_2] + \kappa_{\text{twist}}(k_1 - k_2)^2\}, \tag{2.10}$$

or, in terms of the Gaussian curvature K and mean curvature H,

$$E_{\text{warp}} \approx \tfrac{3}{16}[(3\kappa_{\text{bend}} + \kappa_{\text{twist}})H^2 - (\kappa_{\text{bend}} + \kappa_{\text{twist}})K]. \tag{2.11}$$

This equation is the analogue of the bending energy (2.1). Note that the effective saddle splay modulus for net warping is negative, and usually slightly smaller than the splay modulus. This implies that hyperbolic networks which lie on, or close to, minimal surfaces (such as schwarzites) are favoured over elliptic networks (fullerenes) of similar radius of curvature, a finding confirmed by quantum mechanical calculations (Adams *et al.* 1992).

It is perhaps surprising to note that to this level of approximation the warping energy is independent of the orientation of the net relative to the principal directions on the surface. Although higher order terms do capture this orientation dependence, their effect on the net warping energy is insignificant. The subsequent (quartic) term in the series expansion (2.9) has been calculated explicitly and found to contribute less than 1% of the quadratic term for the carbon systems considered below.

3. Self-energy of fullerenes, buckytubes and schwarzites

The derivation for the self-energy of warped sp^2 carbon networks relies on the accuracy of the simplified form (2.4) describing distortions of the C–C bonds. One parameter, the ratio of the twist to bend moduli, remains to be determined to settle the functional form of the warping energy (2.11), which can be written as

$$E_{\text{warp}} \approx \frac{3\kappa_{\text{bend}}}{16}\left[\left(3 + \frac{\kappa_{\text{twist}}}{\kappa_{\text{bend}}}\right)H^2 - \left(1 + \frac{\kappa_{\text{twist}}}{\kappa_{\text{bend}}}\right)K\right]. \tag{3.1}$$

The reported self-energies, together with the mean and Gaussian curvatures, are given in table 1.

The Gaussian and mean curvatures can be estimated for fullerenes under the assumption that these networks lie on spheres. This assumption can be sharpened to account for the increasingly faceted appearance of higher fullerenes, from the quantum molecular dynamics (QMD) results. For now this is unnecessary. It has been shown elsewhere that for low density sp^2 carbon networks (for which $\langle n\rangle = 6$), the area per sp^2 carbon atom, Ω, is close to 2.62 Å^2, regardless of the network

Table 1. *Data used to compare warping energies of some hyperbolic, elliptic and parabolic graphitic carbon networks with QMD calculations of self-energies per carbon atom relative to a single flat sheet of graphite (far right columns)*

(The designations of surfaces for hyperbolic networks refer to topologically equivalent triply periodic minimal surfaces (the mean curvature, $\langle H \rangle$, of the surfaces covering the networks need not be zero, cf. column 8). The topological index, χ, denotes the Euler–Poincaré index per conventional cubic unit cell for the schwarzite structures. The surface averaged Gaussian curvature is denoted by $\langle K \rangle$. All curvatures are scaled relative to the C–C bond length of 1.42 Å to render them dimensionless. The hyperbolic network densities are equal to the number of C atoms per 'unit volume' of $(1.42)^3$ Å^3.)

net	ref.	surface	χ	N	net density	$\langle K \rangle$	$\langle H \rangle$	warp energy (arb.)	QMD energy (eV)
Schwarzites									
6.82/D	[1]	D	−4	48	0.3147	−0.3641	0	0.0717	0.2080
6.82/P	[1]	P	−4	48	0.2932	−0.3473	0	0.0684	0.4880
	[2]	P	−4	192	0.1667	−0.0946	0	0.0186	0.1900
schwarzite D	[3]	D	−4	216	0.1653	−0.0949	0.1089	0.0255	0.1800
schwarzite P	[3]	P	−4	216	0.1466	−0.0876	0.1047	0.0235	0.2000
	[4]	D	−4	168	0.1840	−0.0759	0.0847	0.0190	0.2200
'foam'	[5]	—	—	—	0.1811	−0.0948	0	0.0187	0.2300
Fullerenes									
	[6]	sphere		60		0.1624	0.4029	0.0609	0.4383
	[6]			80		0.1218	0.3490	0.0457	0.3870
	[6]			80		0.1218	0.3490	0.0457	0.3780
	[6]			84		0.1160	0.3405	0.0435	0.3685
	[6]			84		0.1160	0.3405	0.0435	0.3594
	[6]			84		0.1160	0.3405	0.0435	0.3570
	[6]			120		0.0812	0.2849	0.0304	0.2892
	[6]			120		0.0812	0.2849	0.0304	0.2881
	[6]			120		0.0812	0.2849	0.0304	0.2818
	[6]			140		0.0696	0.2638	0.0261	0.2452
	[6]			180		0.0541	0.2326	0.0203	0.2031
	[6]			180		0.0541	0.2326	0.0203	0.2006
	[6]			240		0.0406	0.2015	0.0152	0.1580
Buckytubes									
perpendicular	[6]	cylinder		10		0	0.2094	0.0251	0.1820
orientation	[6]			12		0	0.1744	0.0174	0.1260
	[6]			16		0	0.1308	0.0098	0.0710
	[6]			20		0	0.1047	0.0063	0.0450
parallel									
orientation	[6]			18		0	0.2017	0.0233	0.1670
	[6]			20		0	0.1816	0.0189	0.1330
	[6]			24		0	0.1514	0.0131	0.0940
	[6]			30		0	0.1210	0.0084	0.0600

The entries in the second column correspond to the following references: [1], O'Keefe *et al.* (1992); [2], Mackay & Terrones (1993); [3], Lenosky *et al.* (1992); [4], Vanderbilt & Tersoff (1991); [5], Townsend *et al.* (1992); [6], Adams *et al.* (1992).

curvature (Hyde 1993*b*), which, assuming a C–C bond length of 1.42 Å, translates to a scaled area of 1.29 ($= 2.6/(1.42)^2$). Now if the fullerene contains N carbon atoms, its radius, R, is given by the approximate expression

$$R \approx \sqrt{\frac{N\Omega}{4\pi}} = \sqrt{\frac{1.29N}{4\pi}}. \tag{3.2}$$

For example, (3.2) leads to a radius of 3.5 Å for C_{60}. The mean and Gaussian curvatures of a sphere are equal to R^{-1} and R^{-2}, respectively, so that the dimensionless curvatures of the fullerenes can be estimated from their carbon number N, alone:

$$\langle K \rangle \approx 9.75N^{-1}, \tag{3.3}$$

$$\langle H \rangle \approx 3.12N^{-1/2}. \tag{3.4}$$

The Gaussian curvature of cylindrical buckytubes vanishes, and their mean curvature is $0.5R^{-1}$, where R is determined by QMD calculations (Adams *et al.* 1992).

The calculation of the curvatures of hyperbolic schwarzite frameworks relies on the beautiful links between topology and geometry, captured in part by Euler's rule for networks, and explained in detail elsewhere (Hyde 1993*b*; Hyde *et al.* 1993). The topology of a surface is conventionally parametrized by the Euler–Poincaré index, χ, which is related to the integral (Gaussian) curvature by the relation

$$\iint_{\text{surface}} K \,\mathrm{da} = 2\pi\chi. \tag{3.5}$$

This remarkable result is the global form of the Gauss–Bonnet theorem of differential geometry.

However, the Euler–Poincaré index is related to the number of faces F, edges E and vertices V in any network which decorates the surface:

$$\chi = V - E + F. \tag{3.6}$$

Consider a single repeat unit of the network, containing N vertices. If all vertices are the nodes of z edges, and the average ring-size in the network is defined by

$$\langle n \rangle \equiv \sum_i \frac{f_i n_i}{f_i}, \tag{3.7}$$

where the sum extends over all ring-sizes, n_i, and f_i denote the number of n_i–rings. Care must be exercised in these calculations, since only those rings that can be continuously shrunk to a single node on the surface are included in the calculation.

Noting that all edges are shared between two vertices, and faces contain on average $\langle n \rangle$ vertices, Euler's relation can be written as

$$\chi = N - \frac{Nz}{2} + \frac{Nz}{\langle n \rangle}. \tag{3.8}$$

This equation, together with (3.5), determines the integral curvature per vertex associated with a z-connected net. Assume again that the surface has average Gaussian curvature $\langle K \rangle$ and that the average area associated with each vertex on the surface is Ω. The average Gaussian curvature is defined by

$$\langle K \rangle = \iint_{\text{surface}} K \,\mathrm{da} \Big/ \iint_{\text{surface}} \mathrm{da} = \frac{2\pi\chi}{N\Omega},$$

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where the integrals are determined over the surface spanning a repeat unit. The average Gaussian curvature can then be related to the area, ring-size and connectivity by

$$\langle K\rangle = \left[2 + \frac{z(2 - \langle n\rangle)}{\langle n\rangle}\right]\frac{\pi}{\Omega}. \tag{3.9}$$

For three-connected structures, such as sp^2 carbon networks, it follows that

$$\langle K\rangle = \left(\frac{6 - \langle n\rangle}{\langle n\rangle}\right)\frac{\pi}{\Omega}. \tag{3.10}$$

It is thus clear that in schwarzites the average ring size must exceed six.

The area per vertex, Ω, can be deduced from the framework density as follows (Hyde *et al.* 1993). The number density of carbon atoms within a volume V is related to the area of the surface A contained within that volume and the area per atom by

$$\rho = \frac{A}{\Omega V}. \tag{3.11}$$

The dimensionless homogeneity index, H, defined by

$$H \equiv \frac{A^{3/2}}{(-2\pi\chi)^{1/2}\, V}, \tag{3.12}$$

together with the Gauss–Bonnet relation (3.5) allows the area per vertex to be expressed solely in terms of the network connectivity (set here to three), density, homogeneity index and ring size:

$$\Omega = \left(\frac{H}{\rho}\right)^{2/3}\left[\frac{\pi(\langle n\rangle - 6)}{\langle n\rangle}\right]^{1/3}. \tag{3.13}$$

This equation allows the Gaussian curvature to be calculated from (3.10), knowing the ring size, density and homogeneity index. Homogeneity indices for various triply periodic minimal surfaces and related surfaces of non-zero mean curvature have been tabulated elsewhere. As a general rule, they are close to 0.75 (Hyde 1993*a*). The scaled Gaussian curvature, required to calculate the warping energy, is $(1.42)^2\langle K\rangle$.

Unlike the Gaussian curvature, the surface-averaged mean curvature of the hyperbolic surface containing the network is not necessarily coupled to the network topology. To estimate this quantity, we calculate the radii of curvature on both sides of the surface from the size of 'collar-rings' which surround tunnels of the hyperbolic surfaces (Hyde 1993*a*). These rings are the complementary set to those included in the calculation of the ring size by (3.7), since collar-rings cannot be shrunk on the surface. If these two radii of curvature are R_1 and R_2, surrounded by collar-rings of size $n^{(1)}_{\text{collar}}$ and $n^{(2)}_{\text{collar}}$, respectively, assume that

$$\frac{R_1}{R_2} = \frac{n^{(1)}_{\text{collar}}}{n^{(2)}_{\text{collar}}}, \tag{3.14}$$

so that

$$\langle H\rangle = \frac{1}{2R_1}\left(1 - \frac{n^{(1)}_{\text{collar}}}{n^{(2)}_{\text{collar}}}\right). \tag{3.15}$$

Since the Gaussian curvature is

$$\langle K\rangle = \frac{1}{R_1 R_2}, \quad R_1^{-1} = \left[\frac{\pi n_{\text{collar}}^{(1)}(6-\langle n\rangle)}{\Omega\langle n\rangle n_{\text{collar}}^{(2)}}\right]^{1/2}. \tag{3.16}$$

The mean curvature is then given by substituting (3.16) into (3.15).

Again, this curvature is rendered dimensionless by multiplying the result by the standard C–C distance of 1.24 Å.

4. Relative energies of some sp^2 carbon networks

Unfortunately, experimental self-energy data for sp^2 carbon networks are sparse, not the least of the obstacles to such measurements being the unfortunate fact that most networks (especially the hyperbolic schwarzites) have yet to be found. However, the next best thing to real data, numerical QMD simulations (Lenosky *et al.* 1992; Mackay & Terrones 1993; O'Keefe *et al.* 1992; Townsend *et al.* 1992; Vanderbilt & Tersoff 1991), offer some test of the simple elastic warping theory developed in the previous section. In order to assess the validity of the model, we have included data for spherical fullerenes, cylindrical buckytubes (the graphitic sheets of which are aligned along two perpendicular directions) and hyperbolic crystalline schwarzites (Mackay & Terrones 1991), as well as a single example of a random hyperbolic foam. The relevant data are summarized in table 1.

5. The validity of the elastic warping energy

It is apparent from figure 1 that the simple form for the warping energy indeed agrees reasonably well with the self-energies calculated for a variety of fullerenes, buckytubes and schwarzites. Note that the self-energy data are themselves subject to the uncertainties of the QMD models, although these are believed to give accurate predictions for sp^2 carbon systems (Adams 1992). Further, the simple functional dependence of bonding energy on bond bending has been noticed before by Schmalz *et al.* (1988) and Adams *et al.* (1992). The latter authors have developed useful phenomenological self-energy formulae for fullerenes and buckytubes. Note that their 'planarity' refers to ideal spherical geometry, as opposed to ellipsoidal geometry (Adams *et al.* 1992). This paper extends that work by including hyperbolic schwarzite data and recasting the self-energy in terms of warping energy analogous to membrane bending energy.

The data for fullerenes, schwarzites and buckytubes overlap most convincingly when the twist modulus is *ca.* 0.05 times the bend modulus. This result is not critical: reasonable fits can be obtained with the ratio of the moduli anywhere between 0 and 0.2. Best fits are obtained for $\kappa_{\text{bend}} = 7.9$ eV and $\kappa_{\text{twist}} = 0.4$ eV per carbon atom. These moduli lead to splay and saddle splay moduli by (3.1), i.e. $\kappa = 4.5$ eV $\approx 190kT$ and $\bar{\kappa} = -1.5$ eV $\approx -65kT$ per carbon atom. These values are typically two orders of magnitude higher than corresponding moduli for amphiphilic membranes.

It is surprising that the magnitudes of the elastic twist and bend moduli for graphitic carbon monolayers can be simply estimated using classical elastic theory for thin plates. According to that continuum theory, the energy of deformation per

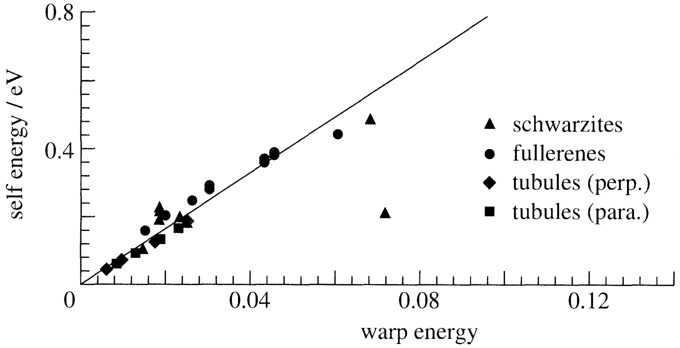

Figure 1. Plot of elastic warping self-energies versus relative energies per carbon atom of fullerenes (Adams *et al.* 1992), schwarzites (Lenosky *et al.* 1992; Mackay & Terrones 1993; O'Keefe *et al.* 1992; Vanderbilt & Tersoff 1991) and buckytubes in two orthogonal orientations relative to the cylinder axis (Adams *et al.* 1992). The data are tabulated in table 1. One adjustable parameter has been used to determine the warping energy: the ratio of the twist to bend moduli. The data are calculated for a ratio of 0.05. The line is an estimated line of best fit; its slope is 7.9 eV, the bend modulus of graphitic carbon sheets.

unit area for a spontaneously flat plate is

$$E_{\mathrm{bend}} = \frac{Et^3}{6}\left[\frac{1}{1-\nu^2}H^2 - \frac{1}{2(1+\nu)}K\right], \tag{5.1}$$

where H and K denote the mean and Gaussian curvatures of the midsurface of the sheet, t the sheet thickness and E and ν are the Young's modulus and the Poisson ratio for the sheet (Fogden *et al.* 1991). Comparison of this form with that of equation (3.1) shows that the ratio of the twist and bend moduli depends only on the Poisson ratio:

$$\frac{\kappa_{\mathrm{twist}}}{\kappa_{\mathrm{bend}}} = \frac{1-3\nu}{1+\nu}, \tag{5.2}$$

and the bend elastic modulus can be estimated as

$$\kappa_{\mathrm{bend}} = \frac{2Et^3}{9(1-\nu^2)(3+(\kappa_{\mathrm{twist}}/\kappa_{\mathrm{bend}}))}. \tag{5.3}$$

The relevant constants for graphite are $E = 10^{12}$ Pa and $\nu = 0.3$. The ratio calculated from equation (5.2) is 0.08, well within the 0–0.2 range discussed in the text.

The magnitude of the bend modulus allows an estimate of the graphitic sheet thickness, t. Taking the bend modulus as 7.9 eV leads to an effective thickness of the carbon sheet of 2.5 Å, which is physically reasonable given that the spacing between carbon sheets in graphite crystals is more than 3 Å.

The apparent validity of the continuum plate elasticity theory for the thinnest possible plate, an atomic monolayer, is perhaps surprising and demands further exploration. Similar conclusions have been arrived at independently by Gamaly & Chadderton (1996).

The significance of the above analysis is twofold. First, it seems that many carbon networks can be modelled as 'atomic membranes', subject to the elastic form for the warping energy of spontaneously flat membranes, derived in generality by Helfrich (1973). Second, this non-Euclidean two-dimensional picture of low-density networks is reasonable, indeed better than a standard three-dimensional approach.

Clearly, this view must eventually break down for sufficiently large curvatures (i.e. high framework densities) of the network, where a three-dimensional approach is more realistic. We suggest that in the case of sp^2 carbon networks, true three-dimensional behaviour is not realized until surprisingly high densities are achieved. The densest case (in the top row of table 1), where the scaled radii of curvature exceed about 0.3 of the C–C bond length, cannot be reconciled with this simple membrane model. This result is consistent with density analyses of a variety of silicate frameworks, which reveal two-dimensional behaviour in all but the densest four-connected framework silicate, coesite (Hyde 1993*b*).

In conclusion, this unconventional theoretical approach to atomic stability offers some insights into common features of molecular and atomic self-assembly. This unification is particularly timely, given the plethora of recent experimental results on mesostructured inorganic materials, templated by molecular assemblies (Huo *et al.* 1994). Stiffnesses of membranes are typically two orders of magnitude lower than the sp^2 carbon systems considered here. Nevertheless, a promising route to fullerene and schwarzite synthesis may lie in such a templating approach.

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