XI. NANOMECHANICS OF GRAPHENE

Carbon is an element of extraordinary properties. The carbon-carbon bond possesses large magnitude cohesive strength through its covalent bonds. Elemental carbon appears in a variety of forms from common graphite to high technology carbon fibers and on to high purity diamond and finally to the modern, ideal nanoscale forms of Fullerenes, nanotubes, and graphene. When Fullerenes (Bucky-Balls) first came into initial exposure and testing, the form was termed by some as "The Molecule of the Year". Later of course it lead to multiple Nobel Prizes. Graphene is the perfect planar form of a sheet of carbon atoms at only one atom of thickness. Fullerenes and single walled nanotubes provide the spherical and cylindrical forms that graphene can take. The planar form, graphene, will be examined here, but it also represents the inherent properties available and exploitable in Fullerenes and nanotubes.

Graphene Nanostructure

Carbon has the atomic number of 6. It has two electrons in an inner shell and four electrons in the outer shell of orbitals. In graphene the four bonding electrons actually form three bonds with nearest neighbor atoms, with one of these being a double bond. The two dimensional nature of graphene then has the atoms

arranged in a hexagonal pattern, as show below in Fig. 1, each with three nearest neighbors. The atomic centers are at the nodes of the pattern and the outer shells of electrons meet midway between nodes.

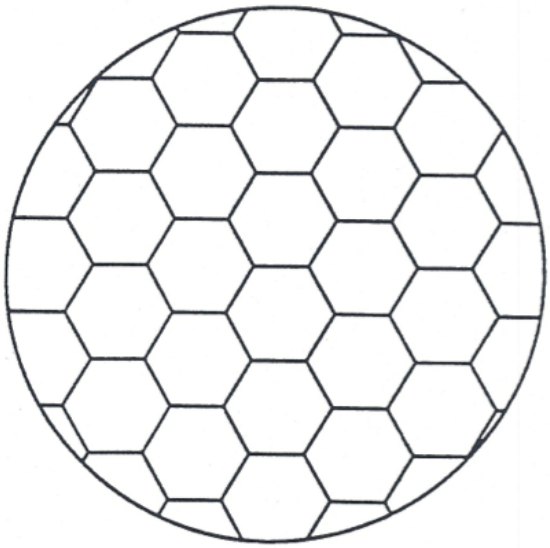

Fig. 1 Hexagonal pattern of graphene atoms

The hexagonal arrangement of the atoms has a six-fold symmetry that assures isotropy of the in-plane, large scale stiffness and compliance properties. In order to model the average stiffness properties of graphene, the hexagonal pattern of atoms is idealized as a hexagonal pattern of connected elastic members that possess axial and bending stiffness characteristics that will be adjusted to represent the bond stretching (and contraction) and the bond bending (distortion) effects. Each individual elastic member between atomic centers is taken with the axial and bending properties specified by the stiffness coefficients

$$k_A = \frac{AE}{l}$$

$$k_B = \frac{12EI}{l^3} \tag{1}$$

where “l” is the distance between atomic centers and the other properties have the usual mechanics designations. Stiffness coefficient k_B is that for the relative displacements of the beam member ends with no end rotations. This overall treatment of the mechanical properties for graphene is motivated by the original conception of Bohr that for some purposes individual atoms could be taken as being effectively elastic bodies.

The hexagonal pattern of elastic members is analyzed to obtain the effective elastic properties of the sheet of carbon atoms. The bending behaviors of the connecting elastic members are represented by Bernoulli-Euler beam theory. At the atomic centers (nodes) the displacements and their first derivatives (slopes) of the members must be compatible and continuous and equilibrium of the forces and moments are required at the nodes (atomic centers). The analysis to ensure the equilibrium conditions is algebraically fairly long, but with no complications or approximations. Thereafter, a homogenization process is applied to average over the complete assemblage of elastic members.

The end results of the analysis are the in-plane elastic properties given by the two dimensional Poisson's ratio, Young's modulus, shear modulus and bulk modulus. These are respectively found to be given by the Poisson's ratio form

$$\nu_{2D} = \frac{1-\kappa}{1+3\kappa} \qquad \left(-\frac{1}{3} \le \nu_{2D} \le 1\right) \tag{2}$$

and the three moduli

$$E_{2D} = \frac{4\kappa}{\sqrt{3}(1+3\kappa)} k_A$$

$$\mu_{2D} = \frac{\kappa}{\sqrt{3}(1+\kappa)} k_A \tag{3}$$

$$K_{2D} = \frac{k_A}{2\sqrt{3}}$$

where

$$\kappa = \frac{k_B}{k_A} \qquad (0 \le \kappa \le \infty) \tag{4}$$

These properties are the controlling, in-plane mechanical properties for the graphene type arrangement of carbon atoms. Since the graphene sheet is only one atom thick there is no characteristic thickness dimension and the three moduli in (3) have units of force per unit length, not per unit area. The limits on Poisson's ratio in (2) are found by letting k_A and k_B in (4) assume all non-negative values.

The single elastic member between two neighboring atoms is taken as shown in Fig. 2 below

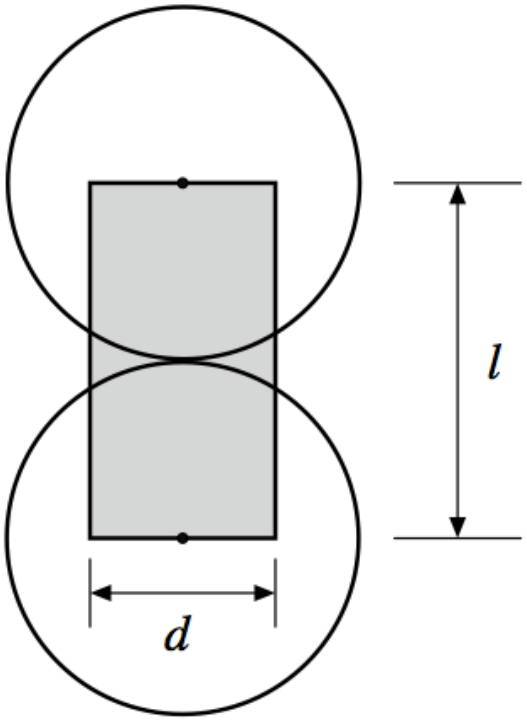

Fig. 2 Idealized elastic member between two neighboring carbon atoms

Appropriate to the two-dimensional nature of the problem for graphene, the elastic members connecting atomic centers are taken as planar forms of length "l" and width "d". The thickness of the elastic members are left as indeterminate and need not be specified here to obtain the variable κ. In this planar case the κ from (1) and (4) becomes simply

$$\kappa = \left(\frac{d}{l} \right)^2 \tag{5}$$

In obtaining (5) the factor of 12 in (1) is cancelled by a factor of 12 for the moment of inertia, I, for the connecting members.

Physically, it is obvious that the elastic member width "d" could not possibly extend beyond the outer shell of the electrons, thus

$$0 \le \frac{d}{l} \le 1 \tag{6}$$

With (5), (6) now becomes

$$0 \le \kappa \le 1 \tag{7}$$

Furthermore, with the physical restrictions (6) and (7) the Poissons's ratio (2) now has the limits

$$0 \leq \nu_{2D} \leq 1 \qquad (8)$$

The case of $\nu_{2D} = 0$ is particularly interesting. This occurs at $\kappa = 1$ which means that the bond stretching resistance is perfectly balanced with the bond bending resistance. Insofar as Poisson's ratio is concerned and in the hexagonal nanostructure, when the two effects are equally sized they counteract each other to produce the value of exactly zero.

It is clear why there cannot be negative values for Poisson's ratios in this case of graphene with its covalent bonding. To allow negative Poisson's ratios would require violation of the physical restriction (6) which would be fundamentally unrealistic and unacceptable. With this new understanding, it is entirely appropriate to say that the positive Poisson's ratios are physically realizable but negative values are not.

The use of Bernoulli-Euler theory for the bending behavior extends up to an aspect ratio of d/l that would not be used with ordinary structural members. But the use here is totally different, with it providing the complete bond bending complement to the bond stretching effect without introducing any additional properties that must be specified independently.

By far the most interesting and most informative property in the group of four properties in (2) and (3) is the Poisson's ratio. Inverting the form (2) to obtain κ in terms of ν_{2D} gives

$$\kappa = \frac{1-\nu_{2D}}{1+3\nu_{2D}} \tag{9}$$

Comparing (2) and (9) it is seen that the relation between ν_{2D} and κ is form invariant. From (2) or (9) and (7) the Poisson's ratio ν_{2D} and the nondimensional bond bending/bond stretching variable κ ranges over the values

ν_{2D}	κ
0	1
1/9	2/3
1/5	1/2
1/3	1/3
1/2	1/5
2/3	1/9

The graph of ν_{2D} versus κ, (2), is given by

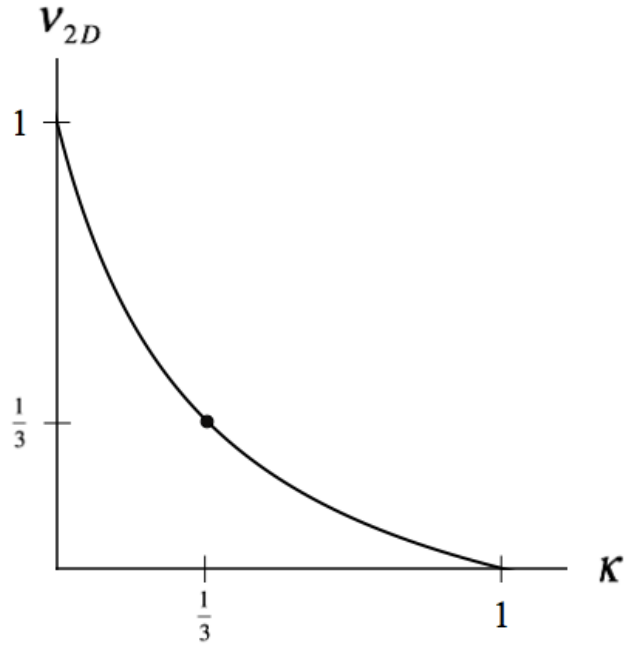

Fig. 3 ν_{2D} versus κ for graphene

It is seen from (2) and (9) that the ν_{2D} versus κ is symmetric about a 45˚ axis that goes through the origin and the central point of

$$\nu_{2D} = \kappa = \frac{1}{3}$$

This value for ν_{2D} and κ has a very special significance. It is at this point that the behaviors of ν_{2D} and κ interchange roles with each other. This is a special turning point or transition point.

There very likely is a change of physical behavior signified by ν_{2D} = 1/3. The terms ductile and brittle cannot be used to describe the change because these terms do not apply here to the perfect arrangements of atoms. Ductile and brittle behaviors usually apply only to macroscopic material behavior controlled by flaws and defects. With this "perfect" material, graphene, perhaps the applicable descriptions would refer to extensibility up to failure such that

$$For \quad \nu_{2D} < \frac{1}{3} \quad Less\ extensibility$$

$$For \quad \nu_{2D} > \frac{1}{3} \quad More\ extensibility$$

This is consistent with the limits at $\kappa = 0$, $\nu_{2D} = 1$ and at $\kappa = 1$, $\nu_{2D} = 0$, The latter case has already been discussed. The former case at $\nu_{2D}=1$ has no resistance to bond bending deformation (bond distortion) and represents behavior reminiscent of elastomers in their 3-D formalism, which allow very large deformations through flexibility of the high molecular weight polymer chains.

Now the question arises as to where does graphene explicitly fit in with this range of conceivable behaviors that follow from this nanomechanics model. Poisson's ratio is difficult to measure directly, but there are clear indications of its likely value or narrow range of likely values for graphene. First of all, diamond is generally considered to have a Poisson's ratio of about $\nu = 0.20$. From Lee et al [1] and Al-Jishi and Dresselhaus [2] there is reasonable evidence that for graphene the Poisson's ratio is somewhere in the range between 0.16 and 0.20. This then places graphene in the range having less extensibility than it would possess if it had a higher value of ν_{2D}, meaning lower value of κ and d/l. For the lower values of ν_{2D}, meaning higher values of κ, the bond bending mechanism in this idealized elastic model suffers non-uniform stress conditions in the idealized beam type members and would be expected to fail at lower extensibilities.

Further application of the moduli in (3) could involve evaluating the coefficient k_A directly from data or atomic scale considerations and then using that along with the other derived properties to examine the other mechanical

properties. It should also be noted that the results in (2) and (3) are the initial, linear range properties, whereas graphene is capable of extending into a considerable nonlinear range of behavior, Lee et al [1].

Comparison with a Hypothetical Nanostructure

The model just derived and discussed for graphene suggests another closely related model for a different ideal, two dimensional arrangement of atoms. Suppose each atom has six nearest neighbors as in the arrangement below in Fig. 4.

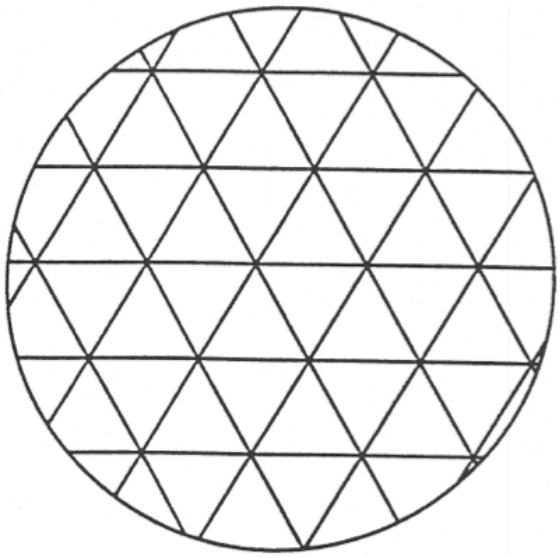

Fig. 4 Triangular pattern of atoms

The basic repeating cell is triangular rather than hexagonal, but the hexagonal symmetry still applies at a larger scale.

There is no known atomic arrangement of elemental atoms that gives this form, but it is an interesting, purely hypothetical nanoscale case to examine here. Each atom would require six bonding electrons (at least) in the outer shell of electrons.

Conducting exactly the same type of equilibrium analysis as that given above for graphene, then gives the governing Poisson's ratio for this new arrangement of atoms as

$$\nu_{2D} = \frac{1-\kappa}{3+\kappa} \qquad \left(-1 \le \nu_{2D} \le \frac{1}{3} \right) \tag{10}$$

where again the limits on Poisson's ratio are found by allowing all possible non-negative values on k_A and k_B in (4).

Between the two nanostructures considered here, then the complete range of Poisson's ratios from (2) and (10) is the usual and accepted range of

$$-1 \le \nu_{2D} \le 1$$

Now using the physical restriction (6) in (5) then (10) has the limits

$$0 \le \nu_{2D} \le \frac{1}{3} \tag{11}$$

for this new nanostructure.

The two nanostructures have the properties shown below with the appropriate physical limits on κ given by (7).

Nanostructure	Hexagonal	Triangular
ν_{2D}	$\frac{1-\kappa}{1+3\kappa}$	$\frac{1-\kappa}{3+\kappa}$
E_{2D}	$\frac{4\kappa}{\sqrt{3}(1+3\kappa)}k_A$	$2\sqrt{3}\left(\frac{1+\kappa}{3+\kappa}\right)k_A$
μ_{2D}	$\frac{\kappa}{\sqrt{3}(1+\kappa)}k_A$	$\frac{\sqrt{3}}{4}(1+\kappa)k_A$

K_{2D}	$\frac{k_A}{2\sqrt{3}}$	$\frac{\sqrt{3}}{2}k_A$

The first nanostructure is that of graphene. The second is the purely hypothetical triangular nanostructure with no presently known atomic configuration.

From the above table it is seen that the bulk modulus K_{2D} is three times larger for the triangular nanostructure than it is for the hexagonal nanostructure at the same values of the bond stretching stiffness coefficients. This is because of the greater number of atomic bonds in the former case. Now express the K_{2D}'s as functions of the ν_{2D} 's for the two nanostructures. Then express E_{2D} and μ_{2D} in terms of the ν_{2D}'s for each nanostructure. These results for the like properties of the two nanostructures at the same Poisson's ratios are also found to differ by the same factor of three as do the K_{2D}'s. Using Poisson's ratio in this manner provides a unification of the results. Poisson's ratio permits and provides a special scaling type of understanding of the behaviors and capabilities of these nanostructures.

Discussion

So far, only the elastic moduli for these nanostructures have been examined. It is not at all clear how the explicit conditions of failure should be approached. Perhaps it is best for these cases of "perfect" materials with no defects or flaws to approach the failure question through atomic scale approaches such as through density functional theory. To the extent that a macroscopic scale form for a failure criterion could be conceived, perhaps the best form for that of two dimensional isotropic behavior would be the polynomial invariants formulation for quasi-isotropic laminates. From Section V, Eq. (5) this failure criterion is

$$\left(\frac{1}{T}-\frac{1}{C}\right)\left(\sigma_{11}+\sigma_{22}\right)+\frac{1}{TC}\left(\sigma_{11}+\sigma_{22}\right)^2+\frac{1}{S^2}\left(\sigma_{12}^2-\sigma_{11}\sigma_{22}\right)\leq 1 \tag{12}$$

where T, C, and S are the failure stresses in uniaxial tension and compression, and in shear. As before, the stresses must have units for force per unit length. Failure matters such as this are completely unexplored. It is generally understood that strength at the nanoscale is not the same critical issue that it usually is at the macroscale.

It is an intriguing question to ask what "clues", if any, these two dimensional ideal materials results may give for the three dimensional engineering materials of common

use. To take a small step in that direction, examine the Poisson's ratios for those elements in the Periodic Table that take the form of solids. The maximums and minimums are given by

Maximum ν	Gold Thallium Lead	0.44
Minimum ν	Beryllium	0.03

In these limit cases, the maximum ν certainly conforms to extreme ductile behavior while the minimum ν material is very brittle. This is consistent with the extensibility results found from graphene and its companion hypothetical nanostructure.

The case of beryllium provides a fascinating example. Brittle though it is, it has spectacular other properties at a very low density. If this material were not so virulently toxic and if it were in reasonable supply, it could well be the material choice for an extremely broad range of applications. Were that to be, it would probably be a very different world in which we live. The present 2-D results show that the exceptionally low value of Poisson's ratio for beryllium likely involves much more of its resistance to

deformation as resulting from bond bending (distortion) than do other materials.

At the other end of the scale, of course dislocations are responsible for ductile behavior, but only correlations with Poisson's ratio are being considered in the present limited context. Thus at one extreme, gold has a very large Poisson's ratio $\nu = 0.44$, implying minimal resistive force due to bond distortion while the other extreme, beryllium at $\nu = 0.03$, has the bond distortion resistance about as great as the bond stretching resistance. In the latter case there results a very high level of stiffness, but at the expense of a very brittle failure behavior. Midway between these two extremes is carbon. For diamond with $\nu = 0.20$ and graphene with $\nu_{2D} = 0.20$ approximately, then from the stiffness coefficients (1) and with the corresponding $\kappa = 1/2$, the bond distortion resistance is half that of the bond stretching resistance. The strength of the bond distortion resistance relative to the bond stretching resistance is one of the fundamental controlling factors that profoundly influences materials behavior. Perhaps it is the single most important effect of all.

With regard to the 3-D Poisson's ratios for the elements, it appears that a gradual transition between ductile and brittle behaviors occurs somewhere in the region surrounding $\nu = 1/5$ (or a little larger). This could be similar to the possible transition in the graphene type hexagonal arrangement of atoms that occurs at $\nu_{2D} = 1/3$. It must be cautioned that these considerations and speculations could only possibly apply to materials forms

for the elements that involve covalent bonding. There are no implications for or extensions to the much more complicated world of materials as alloys, aggregates, compounds etc.

This probe into nanoscale properties provides an important example of the many opportunities that exist at that scale. Although nanoscale failure has little relationship to the usual mechanisms of macroscale failure, the nanoscale is still the logical place to start to understand all of the basic effects. None of the results found here could have been rationalized at the macroscale. In particular, the explicit relationship of the graphene physical properties and the bond bending/bond stretching effects only come into meaningful focus at the nanoscale. The results presented here are new and revealing of fundamental physical behavior for perfect materials formed from carbon atoms.

References

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Al-Jishi, R., and Dresselhaus, G. (1982), "Lattice-Dynamical Model for Graphite", Physical Review B 26, 4514-4522.

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October 11th, 2011