XVII. WHY CARBON BASED MATERIALS ARE SO EXCEPTIONAL AND VITAL

Introduction

There is an old adage that says "diamonds are forever". Frivolous though it may be, there is also a kernel of truth in it. Diamonds are composed of carbon, and carbon is essential to all forms of life. Both figuratively and literally, carbon is the backbone of all organic chemistry including life sustaining DNA. Carbon forms the backbone of most high polymers in the vast technology of plastics. Carbon gives us diamonds, not only of great value as gems, but also of great industrial importance. Carbon is truly forever. The properties, the characteristics, and the capability of carbon in all its various materials forms are anything but frivolous, they are vital and enduring.

One could start by saying that elemental carbon is unique but that doesn't say very much because all of the elements are unique, each in its own way. A more discriminating observation would be that of all of the solids forming elements, carbon is one of the few that has extremely broad usage and application in its purely elemental form rather than as a part of a more complex molecule in a compound or alloy. This is because of the extraordinary mechanical properties of carbon, especially in its diamond form. The other obvious major and profound materials application of an element in its pure form is that of silicon, unique for its electronic properties. Perhaps it is not too surprising to note that there will later be found to exist an intimate connection between carbon and silicon.

As will be shown later, diamond has an elastic modulus, E, (Young's modulus) that is much greater than that of any other solids forming element in the Periodic Table. Only boron and iridium have E's even half as much as that of diamond. All other elements have lower, or much lower elastic modulus values than half that of diamond. Is diamond the perfect material? It's supreme elastic modulus value would seem to indicate yes. But what about ductility? Diamond is certainly very brittle. When one carefully scans the mechanical properties of the elemental materials in the Periodic Table, one finds that there essentially is a trade off between elastic modulus and ductility. Diamond is the highest performer at the elastic modulus end of the

scale while gold is the highest performer at the ductility end of the scale. The price for high modulus is brittleness and the price for high ductility is low modulus.

What about strength? How does it fit in with these considerations of elastic modulus and ductility? The subject of materials failure, commonly called strength, is the prime focus of this website and the related book "The Theory of Materials Failure" [1]. Chapter 8 in Ref. [1] is deeply involved with employing the theory of materials failure to derive the associated theory of ductility.

The theory of materials failure is completely calibrated by the uniaxial tensile and compressive strengths, T and C, where for all homogeneous and isotropic materials

$$0 \le \frac{T}{C} \le 1 \tag{1}$$

The limits in (1) cover an enormous range of different homogeneous and isotropic materials types.

For the specific state of uniaxial tension, the related ductility measure is found to be directly given by

$$D = \frac{T}{C} \tag{2}$$

where

$$D = 0 \quad \textit{Totally Brittle}$$
$$D = 1 \quad \textit{Perfectly Ductile} \tag{3}$$

Although these extremely simple results, (2) and (3), only apply to uniaxial tension, they are perfectly rigorous and the general theory provides the corresponding ductility measures for any state of stress and for any homogeneous and isotropic materials type.

It follows that strength and ductility and the elastic properties all have some controlling relationships and it further follows that these must in part originate from the constitution of the material at the atomic scale. The reason for the "in part" qualification is that flaws and imperfections at all scales also have a controlling effect on the macroscopic strength characteristics of general materials. When examining the tradeoffs between elastic moduli and ductility it would be extremely helpful to eliminate the complication of the effect of flaw structures by considering properties and behavior of the elements in the forms that their associated materials take, namely that of condensed matter. The work here will comply with that specification. If there are flaws or defects, for present purposes they will be taken to occur mainly at the atomic scale, such as dislocations, vacancies etc.

Thus there is no incompatibility in relating macroscopic properties, such as elastic modulus and ductility measures with the architecture at the atomic scale so long as only the elements are under consideration.

There is however one further complication that must be recognized. This is that of the existence of grain boundaries. All of the elements forming solid materials condense into polycrystalline aggregates. Grain boundaries are also a form of materials defects that has a degrading effect on strength. Some elements such as carbon and silicon can also take amorphous forms but these also have imperfect nanostructures because their tetrahedral bonding cannot be formed into perfectly isotropic nanostructures in three dimensions.

There is only one elemental form that is free of all defects. This is that of the two dimensional form of carbon known as graphene. Graphene has perfect hexagonal symmetry with no grain boundaries or other defects. This makes carbon the logical material as a pure element to be used for benchmark studies of mechanical behavior. The comprehensive and ultimately authorative source for all physical and electrical matters for carbon is that of Dresselhaus [2] and the many other carbon related books by the same author.

With the above background and motivation, all of the many different forms of carbon will now be considered and examined in terms of their mechanical properties and related performances. These various material forms include diamond, graphite, graphene, fullerenes, nanotubes, and carbon fibers.

The Element Carbon

Carbon is the 6th element (atomic number 6) in the Periodic Table following hydrogen, helium, lithium, beryllium, and boron. In general, the specific atomic scale characteristics show great order and regularity as the atomic number is increased. But the associated physical properties are just the opposite, showing enormous variability and distinctions as one progresses along in the table. Why are some elements gases and others are solids at some specified condition? Actually, there are solids and liquids and gases, all existing at standard ambient conditions. Interest here resides with the solids forming elements and with the physical properties that are normally considered to be the specific mechanical properties of stiffness and strength.

The first 14 elements of the Periodic Table are shown in Table 1. The atomic number is the number of protons in the nucleus and the corresponding number of electrons orbiting the nucleus. The electrons form into shells and each shell after the first one further divides into sub-shells having different orbital characteristics. The elastic moduli and Poisson's ratios are shown in Table 1 for the solids forming cases along with their crystal structures.

Element	Atomic Number	Electrons per Shell	Orbitals	E GPa	ν	Crystal Structure
Gases H&He	1 & 2	1&2	$1s^1$ & $1s^2$			
Lithium Li	3	2,1	$1s^2\,2s^1$	5	0.43	BCC
Beryllium Be	4	2,2	$1s^2\,2s^2$	287	0.13	HCP
Boron B	5	2,3	$1s^2\,2s^2\,2p^1$	450	0.27	Rhombohedral
Carbon C	6	2,4	$1s^2\,2s^2\,2p^2$	1,050	0.20	Diamond Cubic
Gases N, O, F, Ne	7-10	2,5 to 2,8	$[Be]2p^3$ to $[Be]2p^6$			
Sodium Na	11	2,8,1	$[Ne]3s^1$	10	0.24	BCC
Magnesium Mg	12	2,8,2	$[Ne]3s^2$	45	0.29	HCP
Aluminum Al	13	2,8,3	$[Ne]3s^2\,3p^1$	70	0.35	FCC
Silicon Si	14	2,8,4	$[Ne]3s^2\,3p^2$	170	0.22	Diamond Cubic

Table 1   Elements and properties

Carbon stands out in Table 1 as having the largest elastic modulus value. When examining the entire Periodic Table, carbon still remains as having the largest elastic modulus when in its diamond cubic form. It not only stands out, it stands far above the second largest modulus material, boron, by over a factor of 2. In the broad sense of the term, carbon is singular in its diamond form, it has no competition. If the moduli values are divided by their related density, carbon still retains its dominant position.

Necessarily there is some uncertainty for some of the E and ν values in Table 1. The properties for lithium and sodium as well as beryllium and boron are especially variable (uncertain) based upon many different reported values. But the supremacy of the elastic modulus of diamond is not in any doubt.

The distinctions and variability's in the physical properties of the elements tie in with the orbital characteristics. In Table 1 the s orbital is that where the electron can exist anywhere in the spherical region of the corresponding shell. The 1st shell is full when occupied with 2 electrons and after that the second shell begins to be filled. The second shell is full when 8 electrons are present and after that the 3rd shell is formed and so on.

The orbitals in Table 1 contain not only the s orbitals but also the p orbitals. The notation in Table 1 designates the shell number as the coefficient of s or p and the superscript of s or p is the number of electrons in the orbital of the sub-shell. The p orbitals are more complicated than the s orbitals. The simplest p orbital has 2 lobes in a figure 8 form, rotated about its long axis. It can contain 1 or at the most 2 electrons. Thus it inherently designates directionality. The next more complicated p orbital adds 2 more lobes orthogonal to the first 2. And it thus can contain 2 to 4 electrons and it defines a planar orientation. Finally there can be a p orbital with 6 lobes, which then is three dimensional. It is seen from Table 1 that carbon has a p^3 orbital and thus it may be able to take a planar form in its related bonding with other carbon atoms. This suggests a planar form of carbon, and such an entity does exist, it is graphene. Thus carbon can take the diamond cubic crystal form in 3 dimensions or the graphene planar form in 2 dimensions with hexagonal symmetry.

For the elements in Table 1 of atomic numbers from 7 to 14 the orbital notation uses the symbols [Be] and [Ne] to designate the partial shell configurations of beryllium and neon as being inside those of the orbitals

shown. It should be noted that silicon, as with carbon, contains a p^2 orbital but it has a much more complicated inner shell architecture, also containing an inner p^6 orbital. There is no evidence that silicon can support a 2 dimensional material form as exists with graphene.

These sub-shells with their complex orbitals were deduced through quantum mechanics. It was the triumph of quantum mechanics to put this order into the probabilistic description of the electrons existence and their interactions with the other electrons. Much more complicated orbitals are involved for the atomic numbers above those shown in Table 1.

The Poisson's ratios in Table 1 do not show any apparent ordering or comparative predictability. They are determined by the extremely complex forms of the electrons interacting in the fields created by all of the orbitals.

So the diamond cubic form of carbon stands out in Table 1 and it stands out in the entire Periodic Table. The 2 dimensional carbon form of graphene can also at least be rationalized from the atomic structure of carbon. This then opens the door to all of the standard forms of carbon including fullerenes, and nanotubes. Fullerenes are the spherically curved form of graphene and nanotubes are the cylindrically curved forms of graphene.

Going even further, it is recognized that graphite is the common form of graphene with the weak van der Waal's attractive forces acting between the planes of graphene. Necessarily graphite, as it is normally and naturally found, is dominated by its defects. Carbon fibers obviously have related microstructures that will be taken up later.

Finally, the subject of strength must be introduced. The ideal theoretical strength is often taken to be E/10. This suggests that carbon, and specifically diamond has very high values of strength. However, the subject of strength is far more complex than that of merely having a few simple rules and formulas. Consideration of strength for the various forms of carbon will also be taken up in the following work.

The following work will largely be focused upon diamond and graphene, as representing the 3 dimensional and 2 dimensional forms that carbon can take. High attention will be placed upon the elastic properties for diamond and graphene and how these relate to atomic structure and how these then lead to considerations of strength.

2D and 3D Elastic Properties and Their Limits

For homogeneous and isotropic materials the usual elastic properties are E and ν and/or μ and k, with the latter two being the shear and bulk moduli. Only 2 of these properties are independent. The usual identities relating the 2 pairs of 2 properties are given by

$$\mu = \frac{E}{2(1+\nu)} \tag{4}$$

and

$$k = \frac{E}{3(1-2\nu)} \tag{5}$$

The requirement of positive stored energy gives the limits on Poisson's ratio as being

$$-1 \leq \nu \leq \frac{1}{2} \tag{6}$$

Then it follows from (4) and (5) that:

For $-1 \leq \nu \leq \frac{1}{2}$

$$\frac{E}{3} \leq \mu \leq \infty \quad and \quad \frac{E}{9} \leq k \leq \infty \tag{7}$$

Thus μ and k can take a wide range of values, including being of unlimited size compared with E.

Negative values for Poisson's ratios have never been reported for any of the elements. Under this circumstance then tighter restrictions on μ and k follow as:

For $0 \leq v \leq \dfrac{1}{2}$

$$\frac{E}{3} \leq \mu \leq \frac{E}{2} \quad and \quad \frac{E}{3} \leq k \leq \infty \tag{8}$$

In fact, for homogeneous materials no credible negative values for v have ever been reported and gained acceptability.

For possible application to the elements in general and to diamond in particular, the restrictions (8) must be qualified to apply to polycrystalline aggregates since the diamond cubic crystal is anisotropic. For some elements including diamond there is an amorphous form that preserves the tetrahedral bonding of the carbon atoms but necessarily brings in defects at the nano-scale. So the isotropic forms (7) and (8) apply to either the polycrystalline or amorphous forms of diamond.

Before interpreting the restrictions (7) and (8) it is necessary to develop the corresponding forms for 2D elasticity that allow application to graphene. Since graphene is only one atomic dimension in thickness it cannot be treated as being part of three dimensional elasticity theory. The corresponding 2D elastic moduli must have units of force per unit length, rather than force per unit area. The identities for 2D elasticity corresponding to (4) and (5) are

$$\mu_{2D} = \frac{E_{2D}}{2(1+v_{2D})} \tag{9}$$

and

$$K_{2D} = \frac{E_{2D}}{2(1-v_{2D})} \tag{10}$$

The requirement of non-negative stored energy gives the restrictions on 2D Poisson's ratio as

$$-1 \leq \nu_{2D} \leq 1 \tag{11}$$

This is the 2D counterpart of the 3D restriction (6).

Combining (8) – (10) gives the 2D restrictions on μ_{2D} and K_{2D} as:

For $-1 \leq \nu_{2D} \leq 1$

$$\frac{E_{2D}}{4} \leq \mu_{2D} \leq \infty \quad and \quad \frac{E_{2D}}{4} \leq K_{2D} \leq \infty \tag{12}$$

Again, corresponding to 3D elasticity there is no credible evidence that graphene has a negative Poisson's ratio so it follows that:

For $0 \leq \nu_{2D} \leq 1$

$$\frac{E_{2D}}{4} \leq \mu_{2D} \leq \frac{E_{2D}}{2} \quad and \quad \frac{E_{2D}}{2} \leq K_{2D} \leq \infty \tag{13}$$

Some interesting conclusions follow from the 2D and 3D comparisons of (8) and (13). First for the 2D case, it is seen that the two expressions in (13) coordinate perfectly with each other. That is, the ranges of applicability are completely complementary. It follows from (13) that for non-negative 2D Poisson's ratio

$$\mu_{2D} \leq K_{2D} \quad for \quad \nu_{2D} \geq 0 \tag{14}$$

Relation (14) is a legitimate physical interpretation for the meaning of non-negative 2D Poisson's ratio. The shear modulus must be smaller than the 2D bulk modulus.

In contrast, for the 3D properties in (8) there is overlap between the limits for μ and k. From (8) there follows that

$$\mu \leq \frac{3}{2}k \quad for \quad \nu \geq 0 \qquad (15)$$

There is no obvious and reasonable physical interpretation for (15). The reduced ranges for μ and k in (8) compared with (7) could not be deduced independently and could only come from imposing the restriction $0 \leq \nu \leq \frac{1}{2}$. It follows that μ and k are not the fundamental forms for 3D elastic properties, rather E and ν are the fundamental property forms for homogeneous and isotropic materials, and the non-negative requirement for ν is also a stand alone, meaningful restriction.

This elementary introduction to the significance of Poisson's ratio will later be superseded by reference to more sophisticated and insightful work on its true meaning. But for now, this serves the purpose of showing that Poisson's ratio is of pivotal importance. It is much more than just a routine mechanical property of only secondary importance. It is both the elastic modulus E and the Poisson's ratio ν that will be of importance and significance for both of the major forms of carbon based materials, namely diamond and graphene.

Renormalized Poisson's Ratio

With the understanding that homogeneous and isotropic materials do not allow the existence of negative 2D and 3D Poisson's ratios, some further consequences can be established. Following Ref. [3] it is advantageous to renormalize elasticity theory. With background from [3], the elastic modulus E and Poisson's ratio ν are replaced by the renormalized forms specified by

$$E^* = \frac{E}{1+\nu} \qquad (16)$$

$$\nu^* = \frac{3\nu}{1+\nu} \qquad (17)$$

For v satisfying the non-negative restriction

$$0 \leq v \leq \frac{1}{2} \tag{18}$$

then v^* also satisfies

$$0 \leq v^* \leq 1 \tag{19}$$

With the renormalized properties (16) and (17) the elastic energy takes the especially simple form

$$U = \frac{1}{2E^*} \left[\frac{\left(1-v^*\right)}{3} \sigma_{ii}^2 + s_{ij} s_{ij} \right] \tag{20}$$

where s_{ij} is the deviatoric stress

$$s_{ij} = \sigma_{ij} - \frac{\delta_{ij}}{3} \sigma_{kk} \tag{21}$$

Before examining these results the corresponding renormalized 2D elasticity theory should be recorded. It is given by the renormalized properties

$$E_{2D}^* = \frac{E_{2D}}{1+v_{2D}} \tag{22}$$

$$v_{2D}^* = \frac{2v_{2D}}{1+v_{2D}} \tag{23}$$

where

$$0 \leq v_{2D} \leq 1 \tag{24}$$

$$0 \leq v_{2D}^* \leq 1 \qquad (25)$$

The resulting energy is given by

$$U = \frac{1}{2E_{2D}^*} \left[\frac{\left(1 - v_{2D}^*\right)}{2} \sigma_{ii}^2 + s_{ij} s_{ij} \right] \qquad (26)$$

where now s_{ij} is the two dimensional deviatoric stress given by

$$s_{ij} = \sigma_{ij} - \frac{\delta_{ij}}{2} \sigma_{kk} , \ 2D \qquad (27)$$

and where in 2D the related indices are 1 and 2 only.

Next (20) and (26) will be specialized to the case of uniaxial stress. First for the 2D elasticity case there results from (26)

$$U = \frac{1}{4E_{2D}^*} \left[\left(1 - v_{2D}^*\right) + 1 \right] \sigma_{11}^2 \qquad (28)$$

$$dilatational \uparrow \qquad \uparrow distortional$$

The character of the energy changes completely over the range of possible renormalized Poisson's ratio in (25) as follows:

(i)   For $v_{2D}^* = 1$ there is no dilatational contribution to the energy.

(ii)   For $v_{2D}^* = 0$ the dilatational contribution to the energy is maximized and also balanced with that from the distortional source.

The situation with the 3D elasticity case is somewhat different. From (20) for uniaxial stress there results

$$U = \frac{1}{3E^*}\left[\frac{1}{2}\left(1-v^*\right)+1\right]\sigma_{11}^2 \tag{29}$$

$$dilatational \uparrow \qquad \uparrow distortional$$

In this case the conclusions are:

(i)   For $v^* = 1$ there is no dilatational contribution to the energy.

(ii)   For $v^* = 0$ the dilatational contribution to the energy is maximized but it is not in balance with that from the distortional source.

In comparing the 2D and 3D cases it is seen that they are generally similar but the 2D case has an appealing internal symmetry between the dilatational and distortional sources of energy that the 3D case does not share and possess. As with the results in the previous section, the 3D case is considerably more complex than the 2D case, even on the fundamental sources of the energy.

These results will later be specialized to the 2D case of graphene and the 3D case of diamond. Also, the renormalized properties formulation will be needed in the next section.

Nanomechanics

With the knowledge that only the element carbon can form a two dimensional continuum of atoms, it is logical to examine this carbon constituency from the atomic scale on up. Graphene is the planar hexagonal bonding of carbon atoms. This program was followed in Refs. [4] and [1] and termed to be the nanomechanics of graphene.

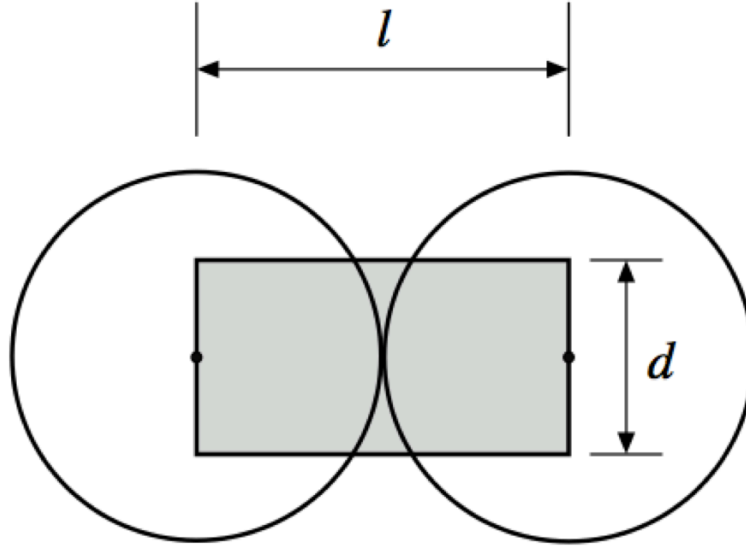The bonding of two carbon atoms is as shown in Fig. 1.

Fig. 1   Bonding of two carbon atoms

The bonding is represented by an equivalent elastic member with the dimensions shown in Fig. 1. The bond bending and bond stretching stiffnesses are designated by k_B and k_A and their ratio is specified by

$$\kappa = \frac{k_B}{k_A} \tag{30}$$

Using two dimensional forms it follows that

$$\kappa = \left(\frac{d}{l}\right)^2 \tag{31}$$

The nanoscale analysis [4] of the hexagonal arrangement of atoms yields the macroscopic elastic properties as

$$E_{2D} = \frac{4\kappa}{\sqrt{3}\left(1 + 3\kappa\right)} k_A \tag{32}$$

$$v_{2D} = \frac{1-\kappa}{1+3\kappa} \tag{33}$$

It is the Poisson's ratio form (33) that will prove to be very useful for 2D graphene. In Ref. [4] a 3D form for all isotropic materials was derived as the counterpart of (33) giving

$$v = \frac{1-\kappa}{2+\kappa} \tag{34}$$

where κ is still given by (30) and (31) but now it represents a rescaled form appropriate to 3D conditions, [3].

The Poisson's ratio form (33) is representative of a specific materials type, graphene, whereas the form (34) applies to all homogeneous and isotopic materials types. In both cases the controlling variable is κ the ratio of the bond bending stiffness to the bond stretching stiffness for whatever element/material is under consideration. The macroscopic property v is solely controlled by this single nanoscale property κ.

The two expressions, (33) and (34) can now be expressed interms of the appropriate renormalized Poisson's ratios. Using (23) and (17) then converts (33) and (34) to

$$v_{2D}^{*} = \frac{1-\kappa}{1+\kappa} \tag{35}$$

and

$$v^{*} = 1-\kappa \tag{36}$$

Both forms (35) and (36) are of significance but (36) is especially important. The nanoscale property κ is linearly related to the macroscopic property form v^{*} as shown in Fig. 2.
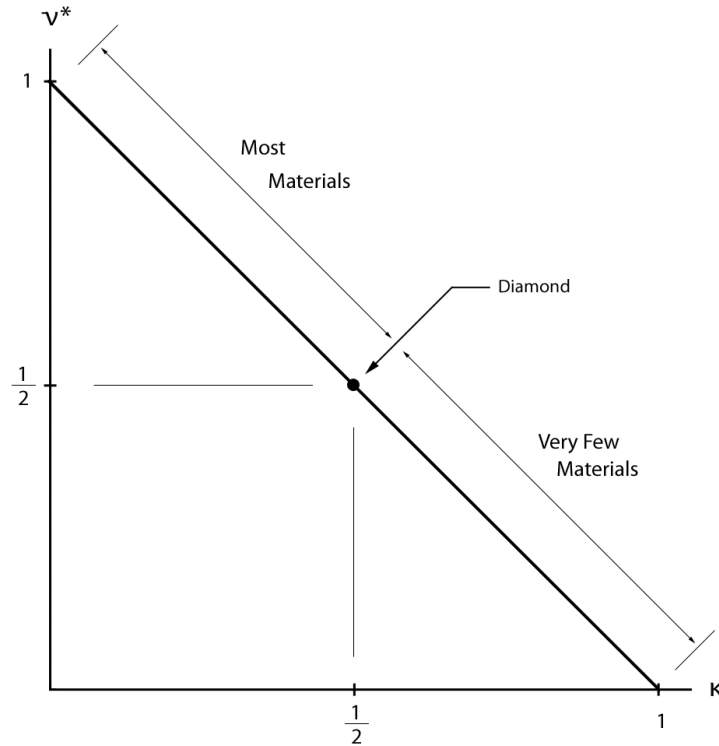
Fig. 2   Macro-scale v^* versus nano-scale κ, (36)

The character of the diamond form of carbon stands out in Fig. 2. Almost all of the elements reside in the region of $\dfrac{1}{2} \leq v^* \leq 1$ in Fig. 2. Furthermore, most homogeneous and isotropic materials exist in the same region. Only the element beryllium and perhaps some ceramics reside in the lower half of the region for v^* shown in Fig. 2.

The value of $v^* = 1/2$ corresponds to the value $v = 1/5$. Although there is considerable uncertainty about the experimental values reported for diamond, the value $v = 1/5$ does seem to be near the most commonly reported values for polycrystalline diamond and for amorphous diamond.

It follows that the Poisson's ratio for diamond lies at or near the extreme lower limit for most materials. Thus carbon in its diamond form not only exhibits the most extreme and maximal value for its elastic modulus, E, its Poisson's ratio also exhibits near extremal behavior. This characteristic is of

great significance because V^* and thereby V gives a window on the nano-scale properties of materials. In particular, through the relation of V^* and K, (36), the value of $K = 1/2$ signifies that of diamond and then (30) gives the corresponding ratio of the bond bending stiffness to the bond stretching stiffness for the carbon atom. As seen in the previous section this characteristic also corresponds to maximizing the dilatational contribution to the total energy compared with that which comes from the distortional source (for most materials).

Although it is not needed here, it should be noted that in Ref. [4] the nano-scale relation between V^* and K was used to prove that Poisson's ratio can never be negative for homogeneous and isotropic materials. This resolves a long standing historical ambiguity, uncertainty, and even controversy.

Poisson's Ratio for Diamond and Graphene

Now a different approach will be taken to establishing the Poisson's ratios for diamond and for graphene. This will be different from anything ever followed before and different from simply appealing to reported experimental values, as was done in the previous section and in [4].

This inquiry into the Poisson's ratios of diamond and graphene begins by asking if the nano-scale form of graphene and the 3D form of diamond have some special compatibility and relationship since both involve the bonding of carbon atoms. And if such a special relationship does exist, how can it be used to advantage? The ratio of stiffnesses in K,(30), is not simply a nano-scale property, is most fundamentally an atomic scale property since it represents the covalent bonding of two carbon atoms in immediate proximity.

The next question would be to ask what macroscopic property could possibly be determined by K and only by K? It must be a nondimensional property since K is nondimensional. Poisson's ratio is the only nondimensional mechanical property that could conceivably fill this role.

As already noted in (33) and (34), the nano-scale theory of Ref. [4] predicts that for graphene

$$v_{2D} = \frac{1-\kappa}{1+3\kappa} \quad \} \quad \textit{Only for carbon in graphene} \qquad (37)$$

whereas for the general 3D case for any material

$$v = \frac{1-\kappa}{2+\kappa} \quad \} \quad \textit{Any element} \qquad (38)$$

In the special case of carbon in (38) it then follows from the previous discussion and deduction that

$$v\Big|_{\substack{carbon \\ diamond}} = v_{2D}\Big|_{\substack{carbon \\ graphene}} \qquad (39)$$

Substituting (37) and (38) into (39) gives

$$\frac{1-\kappa}{2+\kappa} = \frac{1-\kappa}{1+3\kappa} \qquad (40)$$

further determining that

$$\kappa = \frac{1}{2} \qquad (41)$$

Then (41) into (37) and (38) gives the final result that for diamond and for graphene

$$v = v_{2D} = \frac{1}{5} \qquad (42)$$

Thus Poisson's ratio v for diamond is one of the few mechanical properties that can realistically be determined from a´ priori theoretical requirements rather than from direct experimental observation. And the close compatibility of this deduction with the experimental results provides further corroboration and reassurance on the general theory.

In using the equality of V and V_{2D} in (39) it was the only logical choice. E and E_{2D} could not be used for this purpose because they are dimensional and what's more, they don't even have the same dimensions. The other choice would have been to use V^* and V^*_{2D} but they are not basic materials properties, but rather are derivative forms from V and V_{2D}.

The determination that $V = V_{2D} = \dfrac{1}{5}$ thus completes the characterization for diamond. Its elastic modulus E is by far the largest of any element in the Periodic Table. Its Poisson's ratio V is one of the smallest of any element in the Periodic Table. This maximizes or nearly maximizes the stiffening mechanism that comes from the dilatational source of resistance. Its dilatational resistance is quite well balanced with its distortional resistance. Higher values of Poisson's ratio move toward relying just on the distortional resistance mode.

Carbon is unique in allowing the formation of the two dimensional continuum, graphene. The three dimensional form of carbon in diamond is also unique for the mechanical properties that it embodies.

Stress-Strain and Failure

This final section will first examine the elastic stress-strain behavior for diamond and for graphene. Then failure will be taken up, first for diamond. Finally the failure behavior for all forms of carbon materials will be considered, for graphene, graphite, nanotubes, carbon fibers and carbon composites.

In the case of diamond, its stress-strain characterization starts with that in terms of the renormalized elastic properties, E^* and V^*, and it is given by

$$\varepsilon_{ij} = \frac{1}{E^*}\left[\sigma_{ij} - v^*\delta_{ij}\sigma_M\right] \qquad (43)$$

where σ_M is the mean normal stress. This form corresponds to the energy form (20). In the case of diamond, the Poisson's ratio was established to be $\nu = 1/5$ in the last section. From (17) the renormalized Poisson's ratio is then

$$\nu^* = \frac{1}{2} \quad Diamond \tag{44}$$

Using (44) in (43) then gives

$$\varepsilon_{ij} = \frac{1}{E^*}\left[\sigma_{ij} - \frac{\delta_{ij}}{6}(\sigma_{11} + \sigma_{22} + \sigma_{33})\right] \tag{45}$$

Next the corresponding results for graphene will be given. The general 2D elasticity stress-strain form is

$$\varepsilon_{ij} = \frac{1}{E^*_{2D}}\left[\sigma_{ij} - \nu^*_{2D}\delta_{ij}\sigma_M\right] \tag{46}$$

where σ_M is still the mean normal stress, but now in 2D form. The 2D form (46) corresponds to the 2D energy form (26). The Poisson's ratio for graphene from the previous section is $\nu_{2D} = 1/5$ so then from (23) the renormalized value of it is

$$\nu^*_{2D} = \frac{1}{3} \tag{47}$$

Combining (46) and (47) gives

$$\varepsilon_{ij} = \frac{1}{E^*_{2D}}\left[\sigma_{ij} - \frac{\delta_{ij}}{6}(\sigma_{11} + \sigma_{22})\right] \tag{48}$$

Comparing (45) and (48) for diamond and graphene, they are identical except that the former is 3D and the latter is for 2D. Also it must be recognized that E^* and E^*_{2D} for diamond and graphene respectively are different.

To go one step further, consider the three stress states of uniaxial stress, eqi-biaxial stress, and eqi-triaxial stress, all designated by σ. In the case of diamond, (45) gives

$$Uniaxial \qquad \sigma = \frac{6}{5}E^*\varepsilon = E\varepsilon$$

$$Eqi-Biaxial \quad \sigma = \frac{3}{2}E^*\varepsilon = \frac{5}{4}E\varepsilon \qquad (49)$$

$$Eqi-Triaxial \quad \sigma = 2E^*\varepsilon = \frac{5}{3}E\varepsilon$$

The first two forms in (49) are also applicable to graphene with E^* replaced by E^*_{2D} and E replaced by E_{2D}. The third form for the eqi-triaxial condition in (49) has no counterpart for graphene.

In considering failure, first the case for diamond will be taken up. This will be for isotropic diamond in either polycrystalline or amorphous form. The failure criterion is

$$\left(1-\frac{T}{C}\right)\hat{\sigma}_{ii} + \frac{3}{2}\hat{s}_{ij}\hat{s}_{ij} \leq \frac{T}{C} \qquad (50)$$

where

$$\hat{\sigma}_{ij} = \frac{\sigma_{ij}}{C} \qquad (51)$$

and with T and C being the uniaxial tensile and compressive failure stresses. The competitive fracture criterion is

$$\hat{\sigma}_1 \leq \frac{T}{C} \quad if \quad \frac{T}{C} \leq \frac{1}{2} \tag{52}$$

where σ_1 is the maximum principal stress.

In using (50) and (52) the uniaxial strengths ratio T/C must be specified. Although it is difficult to find data on the same diamond types for both T and C, there is common agreement that the value for T is much smaller than that for C due to the inherent flaw structures present in such brittle materials. The T/C values for diamond probably are quite similar to those for glass and higher quality geological materials. This would put the T/C value for diamond about in the range

$$\frac{1}{20} \leq \frac{T}{C} \leq \frac{1}{10}$$

For the purpose of a specific example take

$$\frac{T}{C} = \frac{1}{15} \quad Diamond \tag{53}$$

It is the failure criterion (50) not (52), that controls behaviors for these stress states and the six failure stress levels are found to be given by

$$\begin{aligned}
Uniaxial \quad &\hat{\sigma} = 0.0667 \quad and \quad -1 \\
Eqi-Biaxial \quad &\hat{\sigma} = 0.0351 \quad and \quad -1.90 \\
Eqi-Triaxial \quad &\hat{\sigma} = 0.0238 \quad and \quad -\infty
\end{aligned} \tag{54}$$

The progression to more critical tensile stress states and to more tolerant compressive stress states is evident in (54) as one moves from uniaxial to biaxial and finally to triaxial conditions.

The situation with failure characterization for graphene is more problematic. In considering the possible application of a 2D failure criterion

like (50) to graphene, it would be necessary to measure the compressive strength C. It is not at all clear how this should be done when the continuum is actually an extremely thin layer of only one carbon atom in thickness. More generally, engineering materials have strengths that are predominately controlled by the existence and distributions of flaws, defects, and irregularities. To start with, graphene is not an engineering material and by definition it has no defects. Graphene is the perfect arrangement of carbon atoms in its natural hexagonal pattern. It does not appear to be possible to use the typical mechanics approaches to failure characterization for graphene.

This uncertainty or difficulty does not mean that graphene is exempt from failure. Of course any type of atomic bonding between neighboring atoms can be loaded up to the point at which the bonds fail. It probably is most useful to think of graphene as being loaded in a state of uniaxial tension or eqi-biaxial tension, at least when probing the limits of its ability to carry load. In this case it is not necessary to employ a failure criterion. The failure stress is a scalar, not a tensor, and no multi-dimensional failure criterion is needed.

The testing of graphene was performed by Lee et al [5]. The technique used the atomic force microscope involving nanoindentation with the graphene layer suspended over an open hole. As expected the graphene monolayer exhibited abnormally large modulus and strength with large strains before failure. Although the general stress-strain behavior was nonlinear, the initial linear range used and accommodated a Poisson' ratio of 0.165, [5].

Because graphene exhibits large strain in tensile failure, it would normally be considered to be ductile. Now in previous work, [2], ductility was found to strongly correlated with Poisson's ratios for 3D materials. The value of V_{2D} = 1/5 would seem to indicate a brittle behavior for graphene. However, the error in following that line of reasoning is as follows. The correlation between the degree of ductility and Poisson's ratio is for 3D materials where ductility is primarily influenced by inherent flaws and defects in the material. But graphene is a perfect 2D material and not at all controlled by the same influences that exist with 3D engineering materials, or even with some natural materials as polycrystalline diamond. Graphene is in a class by itself as regards materials strength and ductility.

The comparison between diamond and graphene reveals the full range of behaviors for each and for both in comparison. Both have superior elastic modulus since that property is most directly controlled by the inherent properties of the atomic carbon capability. However, strength is where diamond and graphene become differentiated. Graphene with its perfect nanostructure has a strength capability commensurate with its elastic modulus. Diamond type materials have tensile strength characteristics that are greatly degraded by the flaw structures that exist at all scales. Grain boundaries and other defects exist in polycrystalline diamond while nano-scale and larger defects exist in amorphous diamond. The strength characteristics shown in (53) and (54) directly reflect the degraded tensile strength capability of diamond.

In addition to diamond and graphene, other forms of carbon include fullerenes, nanotubes, and carbon fibers. Fullerenes and nanotubes are the spherical and cylindrical forms of graphene. They are generally taken or idealized to be defect free and thus have the same capability as that inherent in graphene. The properties would be a little different than those in graphene because the bonds in the natural state are deformed to admit the curvature in the two cases. Multi-walled nanotubes add further complications but it still retains its relationship to the essential properties of graphene. There is much work transpiring to bring these forms of fullerenes and nanotubes into the realm of practical, cost effective application.

Carbon fibers are the form of carbon that has made the most spectacular advancements in load bearing applications in recent times. It is dominant when the physical conditions of application require high stiffness and high strength at minimal weight. But it isn't just the fibers, as a single entity, that enables this performance. It is the full partnership of the carbon fibers as embedded in polymeric matrices that produces this nearly unique composite material capability. And the polymeric matrices, such as epoxy at ordinary temperatures and polyimides at elevated temperatures, are in fact carbon based themselves. Virtually all polymers are carbon based.

By themselves the individual carbon fibers have extreme variations in their strength capabilities with the lower ranges being completely unacceptable. But in union with the polymer matrix which bridges across fiber flaws, defects and local misalignments, very high levels of stiffness and strength can be obtained from the combined composite material.

Furthermore the presence of the polymeric matrix phase imparts much needed ductility properties to the composite that would otherwise be severely lacking. Carbon fibers by themselves are extremely brittle.

Yet another form of a carbon based material must be mentioned. That would be graphite. Graphite is essentially "low tech" graphene. The basal planes in graphite are simply single layer graphene. The graphene layers are bonded by weak van der Waals forces to form graphite. Although graphite is common and abundant, it is permeated by flaws and defects. It is also extremely anisotropic. Fused graphite contains weak grain boundaries that also are limiting. When one considers the spectrum of carbon based materials and looks for their aspects of physical commonality one sees that carbon fibers are more or less composed of the graphite architecture but with extremely high temperature forming so that the material at the micro-scale is continuous or semi-continuous. That is, the basal planes of graphite are more nearly continuous, Dresselhaus [2]. This continuity or semi-continuity of the basal planes imparts the superior properties of carbon fibers.

Although carbon fiber nanostructure and microstructure have progressed extremely rapidly over the past 40 or 50 years, there likely is still considerable opportunity for advancement, both in performance levels and cost of manufacture. There is an ever increasing requirement and demand for high performance materials that are light weight. The traditional material form that most nearly fits this picture is aluminum. Perhaps this is partially due to its relatively low atomic number, aluminum is 13 but carbon is even lower at 6. The "new" material form for the same purpose is carbon fiber composites. Carbon fiber composites have superior strength and stiffness compared to those of aluminum and at a considerably lower density. But it costs much more than aluminum to manufacture and to process. So the race is on. That notwithstanding, there will be no losers. There will only be advancements on all fronts with exciting and useful new materials capabilities for and from both carbon fibers and aluminum, as well as from many other materials types.

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