



XII. ARE THE ELEMENTS DUCTILE OR BRITTLE: A NANOSCALE EVALUATION

1 H																	2 He														
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne														
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar														
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr														
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe														
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn														
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Uue	110 Uun																						
																		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
																		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Periodic Table of the Elements

The collection of the elements comprise the fundamental set of constituents, not only for all of nature but for the entire world of creative synthesis. The properties inherent in the individual elements are completely determinative in all of their fascinating combinations and applications. Although there is a broad array of relevant properties for the elements, two of the most important properties are those of stiffness and strength. When strength is brought into the picture, there is always an adjoining consideration and qualification. Is the failure behavior ductile or brittle? This presentation is focused upon seeking a rational method for determining the relative ductility of the individual elements in the Periodic Table, that is for any of those that form solids at ambient conditions. The term relative ductility means relative to the other elements since there is some ambiguity about defining ductility in an absolute sense. Not surprisingly, it will be found that the

element gold provides the “gold standard” for this relative measure of ductility.

A more basic question than that of relative ductility is the following: why are some elements ductile while some others are brittle? This question can only be answered at the atomic or nano scale and it provides the guiding direction to be followed here. What characteristic(s) at the nanoscale determines whether a given element is ductile or brittle and how does this lead to a method for quantitatively assessing all of the solids forming elements on this important issue?

The point of departure is that for the properties of graphene. Graphene is the planar form that carbon atoms can take in forming a layer having only a single atom of thickness. All bonding occurs with and only with the other atoms in the same plane. In this case of carbon, the atoms bond into a hexagonal pattern with the atomic centers at the nodes of the pattern. This case of graphene was studied in Section XI. The method of analysis was as follows. The hexagonal pattern of carbon atoms was represented by a hexagonal pattern of two dimensional elastic members possessing axial and bending stiffnesses. The two associated stiffness coefficients are representative of the bond stretching and bond bending capability between atoms.

With this mathematical formulation it was possible to derive the resulting in-plane elastic properties for the graphene arrangement of carbon atoms. One of the results was the consequent Poisson’s ratio, Eq. (2) Section XI, given by

$$\nu_{2D} = \frac{1 - \kappa_{2D}}{1 + 3\kappa_{2D}} \quad (1)$$

where

$$\kappa_{2D} = \frac{k_B}{k_A} \quad (2)$$

and where k_A and k_B are the axial and bending stiffness coefficients for the hexagonal arrangement of elastic members. The elastic member, of unit thickness, had a width “d” and a length “l” between atomic centers. Then the nondimensional nanoscale variable κ_{2D} was shown to be given by

$$\kappa_{2D} = \left(\frac{d}{l} \right)^2 \quad (3)$$

A particular value of κ_{2D} represents the specific identity of graphene. Further details are given in Section XI.

Interest now is turned to the case of those elements in the Periodic Table that form solids at ambient conditions. In contrast to the two dimensional state of graphene, the elements form fully three dimensional states of matter (materials). Another contrast with graphene is that there is no specific crystalline form that gives isotropic conditions the way that the hexagonal pattern in graphene gives two dimensional isotropy. For the elements, the polycrystalline grains of various symmetries orient randomly to give a state of three dimensional isotropy. Because of these complications it is not possible to directly derive the elastic properties for the elements from a realistic nanoscale architecture, at least not by the same method as that used for graphene. Accordingly, a different, less rigorous, but still quite closely related method will be followed here for the elements.

It is postulated that an expression for the Poisson’s ratio of the elements still has the same form as that given in (1) for the two

dimensional model of graphene, but the coefficients embedded in it would be expected to possibly be very different from the two dimensional case. Thus take for the elements

$$\nu = \frac{1 - \alpha \hat{\mathcal{K}}}{\beta + \gamma \hat{\mathcal{K}}} \quad (4)$$

where

$$\hat{\mathcal{K}} = \frac{k_B}{k_A} \quad (5)$$

In (4) α , β , and γ are coefficients to be determined and $\hat{\mathcal{K}}$ in (5) is the controlling nanoscale variable expressed in terms of the axial and bending stiffness coefficients for the equivalent elastic members connecting atomic centers and simulating the bond stretching and bond bending resistances.

Referring to a pair of bonded atoms, the bond stretching mechanism involves the relative co-axial displacement of one atom with respect to the other. The bond bending mechanism involves the relative tangential displacement between the two atoms. It is the nanoscale variable $\hat{\mathcal{K}}$ involving these two mechanisms that will differentiate the various elements. The form (4), analogous to (1) for graphene, is thought to be well motivated since it will be shown to be easily calibrated by certain known behaviors.

Before proceeding further, it should be noted that the bonding between neighboring atoms is usually but not always completely formed by the sharing of electrons in the outer shell of orbitals. The situation with the stiffness coefficients k_A and k_B is much more complicated. These coefficients represent the bond stretching and bond bending resistances of the atom as a whole and

as such have a dependence upon all the details of all the electronic orbitals and their interactions with each other in deformed configurations. Nevertheless, the aggregated effects embedded in k_A and k_B will provide valuable and sufficient information to proceed further.

Next, standard conditions will be used to evaluate α , β , and γ in (4). The following limits or anchor points must be satisfied

$$v = \frac{1}{2} \quad \text{at} \quad \hat{k} = 0$$

and (6)

$$v = -1 \quad \text{at} \quad \hat{k} = \infty$$

The first condition in (6) is that of no resistance to bond bending and the second case is that of infinite resistance to bond bending. These conditions then reduce (4) to the form

$$v = \frac{1 - \alpha \hat{k}}{2 + \alpha \hat{k}} \quad (7)$$

One coefficient, α , remains to be determined. The form for the elastic members connecting atomic centers will be specified, as shown in Fig. 1.

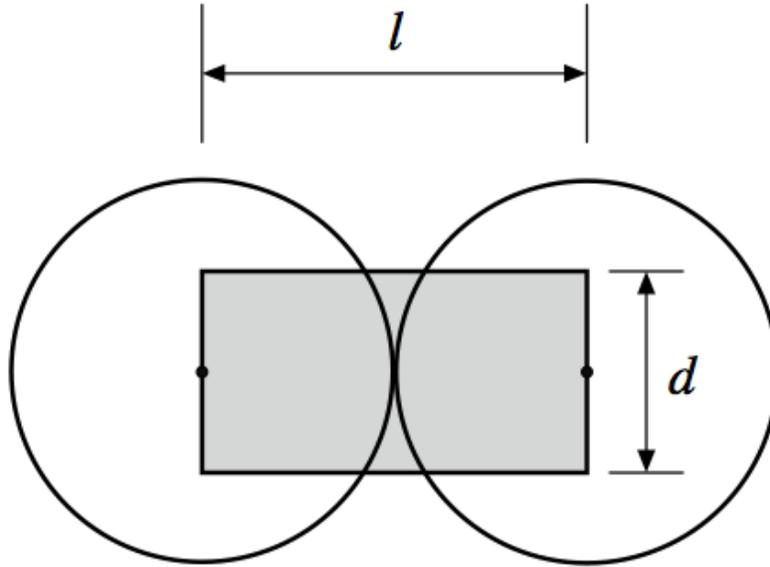


Fig. 1 Equivalent elastic member between bonded atoms

The equivalent elastic member is of circular cylindrical form of radius “ r ”, diameter “ d ” and length “ l ”. The stiffness coefficients for axial and bending stiffness are given by

$$k_A = \frac{A\tilde{E}}{l} \tag{8}$$

$$k_B = \frac{12\tilde{E}I}{l^3}$$

with

$$A = \pi r^2 \tag{9}$$

$$I = \frac{\pi r^4}{4}$$

\tilde{E} is the effective elastic constant for the equivalent elastic member. It should be noted that this entire procedure is mainly a mathematical construct, one that allows a consistent mathematical model to be developed. The concept of the equivalent elastic member is for this purpose only and not an actual, realizable idealization.

Combining these specifications gives the nanoscale variable $\hat{\kappa}$ as

$$\hat{\kappa} = \frac{3}{4} \left(\frac{d}{l} \right)^2 \tag{10}$$

It is convenient to re-scale the nanoscale variable $\hat{\kappa}$ as

$$\hat{\kappa} = \frac{3}{4} \kappa \tag{11}$$

So now

$$\kappa = \left(\frac{d}{l} \right)^2 \tag{12}$$

Finally, following exactly the same course as was found in the analysis of graphene, take

$$\nu = 0 \quad \text{at} \quad \kappa = 1, \quad \frac{d}{l} = 1 \quad (13)$$

This physical requirement states that the elastic member in Fig. 1 cannot extend beyond the outer shell of the electrons and at this condition the related Poisson's ratio is zero. In the case of graphene this condition was derived, not assumed. As with graphene, negative values of ν would require that the equivalent elastic member extend beyond the outer shell of the electrons, $d/l > 1$. This would be physically unrealistic and unacceptable.

Using (10)-(13) gives $\alpha = 1$ in (7) leaving (7) as

$$\nu = \frac{1 - \kappa}{2 + \kappa} \quad (14)$$

This form is the end result of the derivation. It gives the macroscopic Poisson's ratio as a function of the nanoscale variable κ where

$$\kappa = \frac{4}{3} \left(\frac{k_B}{k_A} \right) = \left(\frac{d}{l} \right)^2 \quad (15)$$

The limits on d/l are

$$0 \leq \frac{d}{l} \leq 1$$

and thereby on κ

$$0 \leq \kappa \leq 1$$

Inverting (14) gives

$$\kappa = \frac{1 - 2\nu}{1 + \nu} \tag{16}$$

This form will shortly be shown to be quite recognizable.

It is instructive to compare the three dimensional result (14) with the corresponding two dimensional result (1) derived for graphene. This comparison is shown in Fig. 2.

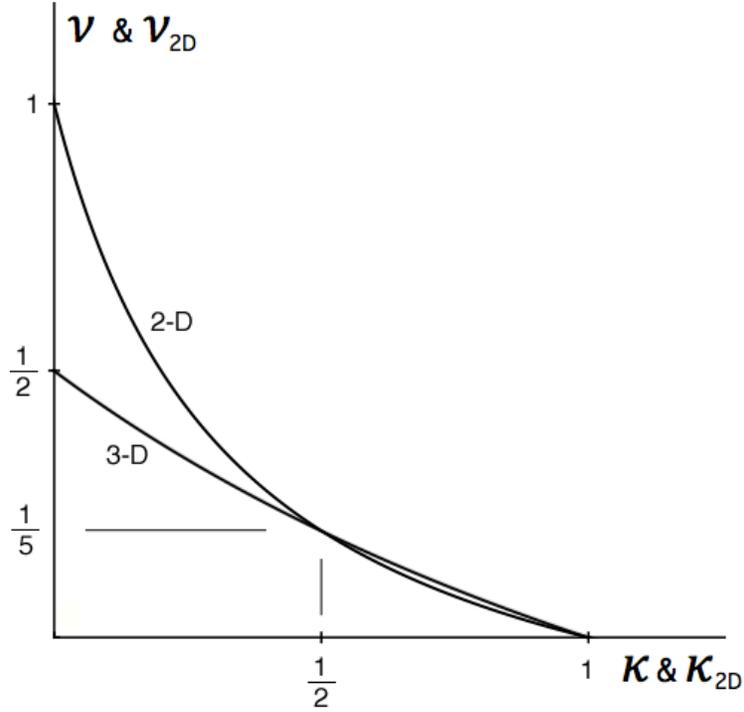


Fig. 2 Comparison of 2-D and 3-D behaviors

From Fig. 2 it is seen that there is something quite special about the value $\nu = \nu_{2D} = 1/5$ with both occurring at $\kappa = \kappa_{2D} = 1/2$, midway between the limits for the physically allowed levels for bond bending and bond stretching.

It is further interesting to compare this behavior with that for the stored energy in an elastic solid. The stored energy can be written as

$$U = \frac{1}{12\mu} \left[\left(\frac{1-2\nu}{1+\nu} \right) \sigma_{kk}^2 + 3s_{ij}s_{ij} \right] \quad (17)$$

where s_{ij} is the deviatoric stress and μ the shear modulus. It is seen that the coefficient of σ_{kk}^2 in (17) requires the value $\nu = 1/5$ when it

is exactly half way between its allowed limits of 0 and 1. Thus the apportionment of energy at the macroscopic scale between dilatational and distortional types is completely in tune with the behavior of the nanoscale apportionment between bond stretching and bond bending, compare the above form for U with the nanoscale result (16).

The physical interpretation of the result (14) is as follows. The nanoscale variable κ ranges between 0 and 1. At $\kappa = 0$ there is no resistance from the bond bending mechanism and from (14) the corresponding Poisson's ratio is $\nu = 1/2$, allowing only shear deformation to occur. For any particular element, as the deformation increases, ultimately it causes yielding and or failure. Near the $\kappa = 0$ limit the deformation can transition into shear localization or dislocation flow or it is simply so great that ultimate failure becomes subsidiary to the excessive shear deformation. This is the case of dominant ductility.

At $\kappa = 1$, from (14) it is found that $\nu = 0$ and the behavior changes fundamentally from that at $\kappa = 0$. First note the form of the stress-strain relations at $\nu = 0$. In terms of principal stresses

$$\begin{aligned}\sigma_1 &= E\varepsilon_1 \\ \sigma_2 &= E\varepsilon_2 \\ \sigma_3 &= E\varepsilon_3\end{aligned}\tag{18}$$

There is no coupling whatsoever between these three relations. The failure behavior is consequently that of the maximum principal stress not exceeding a limiting value. Free standing criteria of this type are generally taken to be reflective of brittle fracture behavior. This behavior at $\kappa = 1$ has the bond bending resistance as about the same size as the bond stretching resistance.

There is no preferred mode of deformation rather than the necessary shear deformation that occurs at and near $\kappa = 0$. This is why the mode of failure changes so drastically between $\kappa = 0$ and $\kappa = 1$.

The failure type expressed as the degree of ductility is taken to vary continuously with the variation of κ , going from extremely ductile to extremely brittle over the range from 0 to 1. It follows from the result (14) that the rank order list of the elements in terms of ascending κ 's is the same as the rank order list of the elements in terms of descending ν 's. Finally, using the Poisson's ratios reported from the testing of the elements permits the construction of the rank order list of the ductility's for the elements. This list is shown below for the more commonly known and used elements that form solids.

Element	ν	Nanoscale κ	Ductility $(1-\kappa)^2$
Absolute Limit, Perfect Ductility	1/2	0	1
Gold	0.44	0.08	0.84
Lead	0.44	0.08	0.84
Niobium	0.40	0.14	0.73
Palladium	0.39	0.16	0.71
Platinum	0.38	0.17	0.68
Silver	0.37	0.19	0.66
Vanadium	0.37	0.19	0.66
Tin	0.36	0.21	0.63
Aluminum	0.35	0.22	0.60
Copper	0.34	0.24	0.58
Tantalum	0.34	0.24	0.58
Titanium	0.32	0.27	0.53
Cobalt	0.31	0.29	0.50
Nickel	0.31	0.29	0.50
Magnesium	0.29	0.33	0.45
Iron	0.29	0.33	0.45
Tungsten	0.28	0.34	0.43
Zinc	0.25	0.40	0.36
Manganese	0.23	0.44	0.31
Uranium	0.23	0.44	0.31
Silicon	0.22	0.46	0.29
Plutonium	0.21	0.48	0.27
Chromium	0.21	0.48	0.27
Carbon (Diamond)	0.20	0.50	0.25
Limit For Most Elements/Materials	1/5	1/2	1/4
Beryllium	0.032	0.91	0.01
Absolute Limit, Total Brittleness	0	1	0

Table 1 Properties for the elements

Table 1 gives the relative ranking of ductility levels for the elements shown by the method developed here, with all cases referring back to the element gold. This method relates the observable macroscopic property ν to the controlling nanoscale variable κ . As such this rank ordering goes by that of the Poisson's ratio values. Most of the above values for ν are taken from "Poisson's Ratio of the Elements" [1], as compiled for the online resource Mathematica from a variety of sources. Only three of the elements shown were not available from this reference. These are carbon, silicon, and manganese. The values for the polycrystalline form of these elements were obtained from other sources that appear to be reliable although there necessarily is some uncertainty.

In basic terms the above table of ductility's is obtained from the nanoscale variable κ which characterizes the relative size of the bond bending and the bond stretching effects. These effects are shown to relate to ductile and brittle failure behaviors. Finally, the relationship between κ and Poisson's ratio allow the actual assembly of the above table. A further consequence of the bond bending/bond stretching behavior κ is that in general the more ductile elements with small κ have lower values of overall macroscopic stiffness whereas the more brittle elements with large's have relatively large stiffnesses. These nanoscale effects provide the explanation of why there is a "trade-off" between high stiffness and high ductility for the elements. Presumably the same can be said of the strength levels.

It must be cautioned that determining Poisson's ratio accurately is a difficult proposition and there could be considerable uncertainty in some of these reported values for ν . Also, it must be

remembered that these are reported values for the elements, not for commercial materials, often of the same common name but with much more complex formulations. Nevertheless, the relative ductility's shown in Table 1 are in reasonable and general accord with common perceptions and observation of ductile vs. brittle behaviors.

The third entry in Table 1 is that of $(1-\kappa)^2$. Nanoscale variable κ goes from 0 to 1 so $(1 - \kappa)$ goes from 1 to 0. Expressing that in a quadratic form, somewhat like energy and some failure forms, then gives a qualified guide to the level of ductility for all the elements in the table, going from perfect ductility at 1 to no ductility, total brittleness at 0. According to this measure of ductility the division between or transition from the ductile elements to the brittle elements occurs about at the elements of cobalt and nickel with $(1 - \kappa)^2 = 0.5$, mid-way between the theoretical limits.

This provisional ductility scale at least gives some sense of the actual ductility levels rather than just the relative rankings. From Table 1 it is clear that only gold and lead are in the extremely ductile class, while only carbon (diamond) is probably in the very brittle class and beryllium is extremely brittle.

As already mentioned, and as evident in Table 1 it appears that the value of the nanoscale variable $\kappa = 1/2$ with the corresponding macroscale variable $\nu = 1/5$ has a very special significance, both for the elements, and possibly for all isotropic materials. Beryllium stands out in the table as a special case, very likely due to its extremely low atomic number. Even so, beryllium is completely consistent with this general ductile versus brittle classification.

The 25 elements in Table 1 are located all over in the Periodic Table although 16 of them are from the transition metals category. The ductility rank ordering in Table 1 does have some correlation with the numbers of shells containing electrons (electronic shells) in the atomic configurations. First, it is observed that the two most ductile elements, gold and lead, have 6 electronic shells each, while the two most brittle elements, beryllium and carbon, have but 2 shells each. The two elements at the transition between the ductile and the brittle elements in Table 1, cobalt and nickel, have 4 electronic shells each.

The actinides, including uranium and plutonium, are in a separate category by themselves. If 3 further elements are temporarily eliminated from consideration, platinum, tantalum and tungsten (all from the 6th Period), then the remaining 20 elements in Table 1 show a quite good correlation between increasing ductility and increasing numbers of electronic shells. This apparent correlation means that increasing the number of electronic shells decreases the nano-scale variable κ that specifies the ratio of the bond bending resistance to the bond stretching resistance. It is not unexpected that these physical characteristics at the atomic and nano-scales could be strongly related.

No doubt many other factors also are necessarily involved to account for each and every individual element. It remains an open question whether any further relationships can be established linking the present rank ordering of ductility's with any of the electronic properties of the orbitals for the elements. There does not appear to be any simple and direct relationship to the valence electrons.

It must be emphasized that this ordering of the ductility's is only for the elements, not for all materials. For more general

materials the use of Poisson's ratio as an indicator of relative ductility levels must be used with caution. Although the procedure may be somewhat useful in general, there would be many important exceptions where the ductility's depend upon many other factors than just the relationship of the bond bending capability to the bond stretching capability for a single constituent in a compound containing many different elements. Flaws and defects would be of decisive importance in general materials.

When one gets into the incredibly broad category of all homogeneous materials, this use of Poisson's ratio to estimate ductility should be replaced by a more finely tuned method for studying ductile and brittle failure. For one thing acknowledgement must be given to the importance of the stress state under consideration. The present approach for the elements probably only applies to the state of uniaxial tension. In Section VII all matters related to ductile and brittle failure are taken up and accessed through the materials type based upon its T/C ratio where T and C are the strengths in uniaxial tension and compression and also where all stress states are considered.

Despite the limitations just discussed as qualifications on this method of characterizing ductile versus brittle behavior, it still gives a remarkable view of the power of nanoscale analysis. In particular, this method has succeeded in relating a non-destructive macroscopic property, Poisson's ratio, to some very important aspects of failure behavior. In so doing it has been found that Poisson's ratio is not just a minor adjunct to the Young's modulus, E , as is often gratuitously implied.

Properties E and ν are equal partners in specifying the controlling properties for all isotropic materials. The dimensional property E mirrors the load bearing capability of the material while nondimensional ν has subtle and vital implications on the

underling nanostructure of the material, especially as regards matters of ductile and brittle failure. To put this another way, for the elements, modulus E represents the aggregated, combined effect of the resistances from atom to atom bond stretching and bond bending, while ν represents and reflects the differences between the bond bending and bond stretching mechanisms.

Reference

[1] “Poisson’s Ratio of the Elements” (2012),
<http://periodictable.com/Properties/A/PoissonRatio.html>.

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