A multiple of 12 for Avogadro

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The new International System of Units may let us select an integer value for Avogadro’s number. Some might prefer an integer that’s divisible by 12, so that an integer number of 12C atoms may be associated (at least to first order) with a gram’s mass. For educational as well as practical reasons it may also help to choose a physically-meaningful definition, within measurement error of the current numeric value. Cubes of diamond face-centered-cubic Si and (much rarer) face-centered-cubic C have been proposed, but these structures don’t have naturally occurring facets (or numbers of atoms generally divisible by 12). We show here that graphite prisms formed by stacking m hexagonal graphene sheets, with m ≡ 51,150,060 carbon-12 atoms on each side, are a natural solution to this challenge.

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I. INTRODUCTION

In redefining the kilogram and Avogadro’s constant, much as the meter was redefined by fixing the numeric value of light speed in meters/second, fundamental relationships will allow one to choose the numeric value of any two of the three quantities: the Planck constant \( h \), the Avogadro constant \( N_A \), and the mass \( M(^{12}\text{C}) \) e.g. in grams or Daltons of a 12C atom. This discussion only applies if one of the two numeric quantities chosen from this list is the Avogadro constant i.e. as a mass-independent number of elementary entities (as well as the number of grams/Dalton regardless of the precise number of Daltons associated with any elementary entity).

One may also still choose either the precise numeric value for \( M(^{12}\text{C}) \) e.g. for a 12C atom to be exactly 12 Daltons, or one may choose the numeric value of Planck’s constant leaving e.g. the mass of a 12C atom to be approximately 12 Daltons subject to experimental refinement downstream. Regardless, if the numeric value of the Avogadro constant is one of the two being chosen for consistency with existing values e.g. to 8 significant figures, this paper discusses physically-meaningful choices for the other 16 (or more) significant figures.

Most likely agree that if we get to select Avogadro’s constant as some number of elementary entities (e.g. atoms or molecules) that it might as well be an integer. For pedagogical purposes in discussing units for mass, it might also help to make that integer divisible by 12 e.g. so that one gram is to first order the mass of an integer number of 12C atoms.

One human-centered strategy for doing this might be to require as few significant decimal digits as possible to specify the constant, since most humans use base-10 numbers. In that context, for instance, \( 6.02214150 \times 10^{23} \) is an integer divisible by 12 that would serve admirably.

The other strategy is to choose the number of atoms in a relevant physical structure, to make the definition concrete. Cubes of simple-cubic and face-centered-cubic Carbon4, and of diamond face-centered-cubic Silicon3, have for example been proposed in this context.

The major problems with these choices are that: (i) simple-cubic carbon doesn’t exist in nature, (ii) fcc carbon is at best rare5,6, (iii) none of these structures have naturally-occurring facets, during growth or cleavage, that lie on the (100) planes which bound these cubes, and (iv) symmetry does not dictate that the number of atoms in these structures is divisible by 12.

We show here that none of these problems exist for the most stable form of carbon under standard conditions, namely hexagonal graphite. Moreover, graphite is constructed from graphene sheets whose controlled synthesis at the atomic-scale is likely to see great progress by nanotechnologists in the years ahead. If any macroscopic object will be possible to assemble from a chosen number of atoms in the decades ahead, this may be it.

II. GROWING GRAPHENE

Our examination of graphene structures begins with a Mathematica program designed to examine the dendritic crystallization of unlayered graphene from a non-equilibrium melt, as one possible mechanism to explain
the unlayered-graphene cores found in a subset of the pre-solar graphite onions (obtained from primitive meteorites) whose isotopic composition indicates condensation in the atmosphere of asymptotic giant branch stars (which nucleosynthesize the lion’s share of carbon in the universe).

Although the program is designed to add carbon atoms also to sheets with defects, in this context we’ve simply added carbon atoms to a flat “graphene seed”. If Fig. 1 we start with 24 atoms bounded by one pair of external atoms on each of the 6 sheet-sides for $2 \times 6 = 12$ surface atoms with only two bonds and 12 internal atoms with 3 bonds each. This beginning state has $6 + 6 + 12 = 24$ atoms.

The first growth step adds three external atoms to each pair, leaving us now with 24 internal atoms and $3 \times 6 = 18$ surface atoms for 42 atoms total. The sequence of additions now looks like $6 + 6 + 12 + 18 = 42$.

The second growth step adds a singly-bonded edge atom and two doubly-bonded edge atoms for each of the 6 previous surface pairs. Now there are 42 triply-bonded internal atoms, $6 \times 2 = 12$ doubly-bonded surface atoms and $6 \times 1 = 6$ singly-bonded surface atoms for a total of 60 atoms. The sequence here is $6 + 6 + 12 + 18 + 18 = 60$.

Finally we add 4 doubly-bonded surface atoms on each side. Now there are 60 triply-bonded internal atoms, and $6 \times 4 = 24$ doubly-bonded surface atoms with a total of 84 atoms in the same closed-shell arrangement of the starting sheet. The sequence is now $6 + 6 + 12 + 18 + 18 + 24 = 84$.

One possible pattern of atom-increments is $(0) + 6 + 6 + (12) + 18 + 18 + (24) + 30 + 30 + (36) + 42 + 42 + (48)$ etc. The totals would then read $(0), 6, 12, (24), 42, 60, (84), 114, 144, (180), 222, 264, (312)$ etc. Jumping only between the closed shells in parentheses, the total number of carbon atoms goes from 0, 24, 84, 180, 312, 480 etc. with 0, 6, 12, 24, 36, 48, 60 etc. "sheet-surface" or edge-atoms respectively.

The closed-shell recurrence relation therefore looks like $N_{n+1} = N_n + 3S_n + 24$, where $S_{n+1} = S_n + 12$. From this, it looks like closed shells with $n$ atom-pairs along each of 6 sides ($2n$ "surface atoms") have a volume of $N_{\text{hex}} = 6n(1 + 3n) = 3n + 9m^2/2$ carbon atoms with $S_{\text{hex}} = 12n = 6m$ atoms on the 2D surface (the hexagonal sheet edge), in terms of the number of atom-pairs $n = 0, 1, 2$, etc. and the number of atoms $m = 2n = 0, 2, 4$, etc. on each side.

### III. STACKING HEXAGONS

There likely exists an even-integer number of $m$ graphene-hexagons in a graphite stack, such that $m$ atoms on each hexagonal sheet-side yields a number of carbon atoms closest to our standard value for Avogadro’s number. The even-integer choice of $m$ for atoms on the side of a closed-shell sheet comes from their natural pairing along the sheet edges, while the even-integer choice of $m$ for number of sheets arises from symmetry considerations because the unit cell is two-layers thick in the (002) direction as shown in Fig. 2.

The number of atoms in an $m \times m$ hexagonal prism, constructed in this way, is:

$$N_{\text{total}} = mN_{\text{hex}} = 3m^2 + 9m^3/2. \quad (1)$$

If $m = 0$, the $N_{\text{total}} = 0$. If $m = 2$, $N_{\text{total}} = 2 \times 24 = 48$ atoms. If $m = 4$, $N_{\text{total}} = 4 \times 84 = 336$ atoms, etc.

Although it may not be obvious from the equation above, $N_{\text{total}}$ will always be divisible by 12. One can see this from our physical model by pointing out that any structure with even $m$ can separated into two equal layer-sets, each of which in turn (by symmetry) can be divided into six equal pie-slices. Mathematically, this is
FIG. 3: Possible factors for Avogadro’s number as a physically-realizable number of carbon atoms, divisible by 12.

true since \( N_{total}/12 = (m/2)^2(1+3(m/2)) \) is an integer if \( m \) is even.

Of course we are looking for \( m \) such that \( N_{total} \Rightarrow \) Avogadro’s number. For example a faceted graphite-crystal with a set of \( m \) (002) graphene sheets, each of which has \( m \) atoms along the sheet hexagonal edges that make up the 6 {110} facets, would for \( m = 51,150,060 \) have 602,214,158,510,196,804,982,800 atoms which compares nicely to current approximations.

The result of this choice for \( m \) is closer to \( 6.0221415 \times 10^{23} \) than is the best (but non-realizable simple-cubic) model compared to it in the Fox article about Carbon cubes. It is also closest of the those proposed models to the value of \( 6.02214179 \times 10^{23} \) recommended here. Subtracting 2 from this value of \( m \) will put it closer to the lower value of \( 6.02214078 \times 10^{23} \) based on Si-28 measurements here.

This crystal would be about 1.71 cm thick, and have a (circumscribed-cylinder) diameter (twice the length of one side) of about 2.18 cm. A hexagonal prism like this is already approximately one-mole of carbon. If the physical model discussed here is used to redefine Avogadro’s number, to the extent that Carbon-12 has a mass at or near 12 Daltons then one gram would be near if not equal to the mass of \( N_A/12 = 50,184,513,209,183,067,861,900 \) atoms of \(^{12}\text{C} \) as well.

The divisibility of this suggested integer is related to its high factorability. As shown in Figure 3 the factors include five factors of 2 and five factors of 3. The hex-prism layer/side integer \( m = 51,150,060 \) is also relatively factorable, with two factors of 2, two of 3, and one each of 5, 13 and 21859.

IV. DISCUSSION

The Avogadro constant is in essence a conversion factor between atom-scale and macroscopic units. Its scale size is therefore specified to many significant figures historically, by the relationship between macroscopic and atomic units of mass. If the new-SI allows us to select an exact value for this constant, there may be scientific and pedagogical value for using a physically-meaningful model.

The scientific value, for example, might be found in our ability to construct and maintain precise molar/mass standards by simply counting the number of atoms (e.g. with an electron microscope) to make sure all atoms are still there before putting the standard to use. Carbon and its graphite/graphene structures are already among the most intensely-studied by nano-technologists, and the most stable at least in the absence of hot oxygen or molten iron.

Independent of our ability to manufacture and maintain 12-gram (or much smaller) graphite standards which contain a precise number of moles of \(^{12}\text{C} \), on the pedagogical front one can certainly build graphite and "pretend-graphite" models of the hexagonal prism. Figure 4 illustrates with an \( m = 4 \) hex-prism, with a form-factor similar to that of the \( m = 51,150,060 \) version. This can be constructed in the rescaled size of the Avogadro’s number prism using today’s 3D printing technology.

If the prism is made of graphite, or a substance with density comparable to graphite, then it will give folks a concrete idea of the space taken up by a mole of condensed matter as well as the weight of a mole of car-
bon. The weight of a mole of other atoms will be proportionally heavier or lighter according to the ratio between atomic weights.

The space taken up by a mole of matter for most solids and liquids will be a bit larger than this because of the high atomic density of graphite ($\approx 1.13 \times 10^{23}/\text{cc}$), but not by much since e.g. the number of atoms per cubic centimeter in elemental solids and liquids is around $(4.70 \pm 2.56) \times 10^{22}$. Equivalent sphere radii (which go inversely as the cube root of density) show even less variability, with a standard deviation less than 20 percent of the mean.

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