

REMARKS UPON AN ELEMENTARY PROBLEM IN STEPWISE NETWORK CONSTRUCTION.

E.C. Kirby

Resource Use Institute

14 Lower Oakfield, Pitlochry, Perthshire PH16 5DS, Scotland UK

Abstract. The principles of a possible algorithm to convert a set of empty vertices into a 3-valent network, by inserting one edge at a time, are outlined, but a serious practical problem is pointed out as an open question; namely, are there reasonably simple conditions that will ensure that every vertex in the set is incorporated into an arbitrary planar network with its valency of three fully satisfied?

INTRODUCTION

Construction of large chemical molecules, whether in the literal sense pertaining to the physical world of nature and synthetic chemical laboratories, or figuratively in the context of diagrams and codes, is normally done in a planned and systematic way. Attempts are made to build up the structure from chemical building blocks in accordance with a sequence of known or suspected rules of chemical behaviour. There are, however, some structures or states that arise from repeated operations of a very simple kind. Examples are polymerization reactions, where in the presence of a catalyst small monomers assemble themselves into macromolecules, and crystallization processes.

Here we think it interesting at least to consider the possibility of this happening in the generation of fullerenes. These all carbon structures, consisting of boundless networks of 3-valent carbon atoms closed upon themselves in 3-dimensional space have been made in

various spheroidal,[1] tubular[2, 3] and possibly toroidal forms,[4-7] and much research is active in this area. See references [8-28] for a small and arbitrary selection of recently published papers.

So, suppose we want to think about accretion processes within a cloud of condensing carbon vapour - a situation where fullerenes might well arise. The behaviour of such a system can be simulated, albeit in oversimplified form, by the process of edge addition to a disjoint graph that starts simply as a set of unconnected vertices. Here, however, we are not much concerned with discussing the results in detail. We wish merely to point out a problem with this approach - which in itself is of some interest

The task is this: Given a set of vertices representing atoms, to introduce edges to produce a connected network, but one that everywhere is locally planar, not one that is 'tangled up'. Then, how can we ensure that a connected graph of a specified size and genus is produced?

METHODS

The Planarity of The Network.

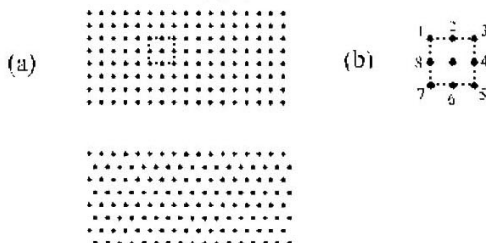
To ensure local planarity it is best to specify that a bond/edge can be inserted between two vertices only when are near neighbours (and this is a reasonable assumption for chemical interaction anyway). Since we start with unconnected vertices, this immediately implies that we are not dealing with a purely graph-theoretical problem, but one that also has geometric aspects. An assembly of three-valent carbon prefers to be planar, and as we wish to model such a network, we will simplify the starting conditions by assuming that all vertices are coplanar.

We can now simplify further by assuming that the vertices form a regularly spaced array. The erratic variation of geometric distance by thermal motion may very simply be mimicked by conducting edge formation in a partially or wholly erratic sequence. Horizontal rows of vertices may be set to have aligned or staggered vertical columns, the former being somewhat simpler to deal with. Every vertex will thus have up to eight neighbouring vertices in its immediately surrounding 'shell' (Figure 1a). If we set two rules,

1. Vertex i may bond to vertex j only if j belongs to the 'shell' of i , and

2. Vertex j may be at any of the eight shell positions, but both i and j must be of no more than degree-2, and no crossing of a previously made bond is allowed (see Figure 1b), these will ensure that, locally, the network is always planar.

Figure 1. Possible starting graphs for network construction.*



*(a) Two arrays of empty vertices used as described to start construction of a network and (b) a vertex and its shell of labelled neighbours. Subject to a maximum valency of three, this vertex can connect to any vertex 1-8, provided that the connection does not cross an existing edge.

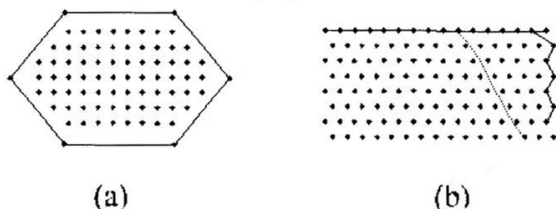
The Overall Topology

Often it is convenient to predefine this, and this can be done by giving attention to vertices on the perimeter first. The only practical difference between a finite, geometrically planar network and a polyhedron is that in the latter all faces are of roughly comparable size, whereas a planar sheet will usually have one (forming the perimeter) which is significantly larger than all the others. It follows that if an enclosing ring of appropriate size, say five, six or seven vertices is drawn, and all other rings are of a approximately similar size, then a polyhedron is guaranteed. (See figure 3a)

Ensuring a toroidal structure (genus 1) is slightly more complicated. Here the enclosing ring of perimeter vertices should be partitioned into four, and alternate opposite pairs connected across the vertex-populated space in apparent violation of rule 1 above, as shown in figure 3b. This is only an *apparent* violation because, when these vertex pairs are treated as if on the face of a torus, they are in fact near neighbours of each other. For a Klein

bottle, one pair of opposite sides can then be paired in reverse order. These 'round-the-tube' connections can of course be made after creating the main network, by insertion.

Figure 2. Examples of edge sets installed to guide the network toward particular topologies*



*For, in this case (a) a polyhedron, and (b) a torus. Dotted lines show connections that are recorded, but which can be crossed - because in a conventional 3D realization they would not be in same plane as the empty vertices shown.

The next stage is to populate the enclosed area with unconnected vertices, and then install connections as described earlier.

THE PROBLEM

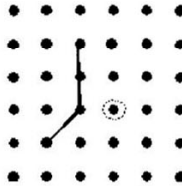
Everything described up to now is comparatively simple to incorporate into an algorithm, which can use random methods, or some additional, more systematic, set of rules. So what is the problem with this approach? It lies in the difficulty of incorporating all the vertices into the connected 3-valent network. Figure 3 exemplifies a common aberration, where a single (degree-0) vertex becomes isolated, because it is surrounded by vertices that already are all of degree-3. The same thing can happen to a degree-1 or degree-2 vertex, or indeed to a whole substructure. If, on the other hand, one relaxes the connection rules, the clear assurance of planarity is easily lost. It should be noted that marooning of degree-0 vertices is a problem only for graph-theoretical construction. In a real assembly of reacting carbon atoms it would probably be irrelevant (assuming that none became trapped within a cage). On the other hand, the 'locking in' of degree-1 or degree-2 vertices as part of the network itself, is a potential problem in both cases.

DISCUSSION

It seems to be an open question as to whether there is any rule set of reasonable simplicity which reconciles these requirements, i.e. to generate a cubic network of specified size, by sequential edge installation, that everywhere is locally planar.

This problem is strongly reminiscent of how error prone is the task of finding a Hamiltonian path by tracing through a polycyclic network where, again, it is all too easy to reach a situation where completion is impossible.[29, 30] Another related practical difficulty is that it is very easy to set a lower limit on the size of ring allowed, by designing a test that refuses to accept a connection creating such a ring, but much more difficult to set an upper bound.

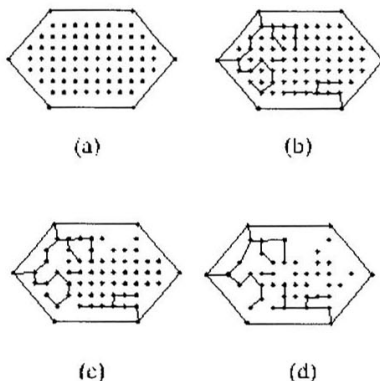
Figure 3. The problem of 'marooning'.*



*The ringed vertex shown cannot, under the rules set, be connected to any of its neighbours because their valencies are already saturated. Besides empty vertices, the same situation can occur with any vertex of degree < 3 , and for a disjoint subgraph.

These remarks do not of course invalidate the procedure as a method of obtaining a structure of the required topology and connectivity, but they do mean that the size of the system is unpredictable. (Although, with random edge installation, statistical estimates may be made). It is a simple matter to finish off an incomplete network by pruning, i.e. by deleting zero-, one- and two-valent vertices, and deleting or reassigning their bonds (Figure 4).

Figure 4. An example of polyhedron formation.*



*(a) In this case an outer hexagon has been connected inwards to an array of free vertices. (b) Edges have been installed, but free vertices remain. Note that some of these could be connected were the operation continued further, while some are now locked into the disjoint state. (c) Free vertices have been deleted. (d) Finally, all vertices below degree-3 are eliminated by pruning and contraction to give a polyhedron with 46 vertices and 25 faces, varying in size from 4 to 8.

One partial solution to this problem of 'vertex marooning' is to start from a Hamiltonian path or cycle, and then to add cross connections to form the faces. Care must still be taken, but mistakes are less easily made. However, the Hamiltonian problem is itself a difficult one.

Thus far we have described the insertion of edges only. Results are much more predictable if insertions of simple graph fragments, such as K_2 and the trimethyl graph between edges are allowed, and this process is studied in more detail elsewhere.[31]

CONCLUSIONS

So far there is no ideal sequential method of construction. These simple methods which start by edge insertion between vertex pairs are very convenient for use in an algorithm, but, as currently formulated do not allow exact sizes to be made reliably.

We pose as a practical open question whether an array of empty vertices can efficiently and reliably be converted to an arbitrary locally planar cubic network in stepwise fashion using all the vertices.

REFERENCES

- [1] H. W. Kroto, J. R. Heath, S.C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **1985**, 318, 162-163.
- [2] P. W. Fowler, *Journal of Physics and Chemistry of Solids*, **1993**, 54, 1825-1833.
- [3] J. Aihara, T. Yamabe, and H. Hosoya, *Synthetic Metals*, **1994**, 64, 309-313.
- [4] T. G. Schmalz, W. A. Seitz, D. J. Klein, and G. E. Hite, *J. Am. Chem. Soc.* **1988**, 110, 1113-1127.
- [5] R. Tosi and S.J. Cyvin, *Zbornik radova Privodno-matematickog fakulteta*. Univ. Novom Sadu, **1992**, 22.
- [6] E. C. Kirby, R. B. Mallion, and P. Pollak, *J. Chem. Soc. Faraday Trans.* **1993**, 89, 1945-1953.
- [7] Jie Liu, Hongjie. Dai, Jason.H. Hafner, Daniel.T. Colbert, Richard.E. Smalley, Sander. J. Tans, and Cees. Dekker, *Nature*, **1997**, 385, 780-781.
- [8] F. T. Edelmann, *Angewandte Chemie International Edition*, **1999**, 38, 1381-1387.
- [9] Tomislav Dosli, Poster presented at *Math/Chem/Comp* **1999**, Inter University Center, Dubrovnik, Croatia; personal preprint, 1999.
- [10] Z. Slanina, X. Zhao, and E. Osawa, *Relative Stabilities of Isomeric Fullerenes*, in *Advances in Strained and Interesting Organic Molecules, Vol 7 1999*, B. Halton, Editor. 1999, Jai Press Inc: 100 Prospect Street/Stamford/CT 06901-1640/USA. p. 185-235.
- [11] P. M. Ajayan, *Chemical Reviews*, **1999**, 99, 1787-1799.
- [12] G. G. Cash, *Fullerene Science and Technology*, **1999**, 7, 733-741.
- [13] G. Brinkmann, P. W. Fowler, D. E. Manolopoulos, and A. H. R. Palser, *Chemical Physics Letters*, **1999**, 315, 335-347.
- [14] N. Martin, L. Sanchez, and D. M. Guldi, *Chemical Communications*, **2000**, 113-114.
- [15] G. Mehta and P. V. V. S. Sarma, *Chemical Communications*, **2000**, 19-20.
- [16] R. N. Kostoff, T. Braun, A. Schubert, D.R. Toothman, and J. A. Humenik, *Journal of Chemical Information and Computer Sciences*, **2000**, 40, 19-39.

- [17] M. Deza, P. W. Fowler, A. Rassat, and K. M. Rogers, *Journal of Chemical Information and Computer Sciences*, **2000**, 40, 550-558.
- [18] E. C. Kirby, *Recent Work on Toroidal and Other Exotic Fullerene Structures*, in *From Chemical Topology to Three - Dimensional Geometry*, A. T. Balaban, Editor. 1997, Plenum Press: New York. p. 263-296.
- [19] C. G. Cash, *Journal of Chemical Information and Computer Sciences*, **1998**, 38, 58-61.
- [20] E. C. Kirby and P. Pollak, *Journal of Chemical Information and Computer Sciences*, **1998**, 38, 1256-1256.
- [21] P. E. John, *Croatica Chemica Acta*, **1998**, 71, 435-447.
- [22] D. Burago and S. Ivanov, *Geometric and Functional Analysis*, **1998**, 8, 783-787.
- [23] M. F. Lin, *Physica B*, **1999**, 269, 43-48.
- [24] M. F. Lin, *Journal of the Physical Society of Japan*, **1999**, 68, 3744-3745.
- [25] Patrick W. Fowler, Peter E. John, and Horst Sachs, *DIMACS Series in Discrete Mathematics and Theoretical Computer Science*, **2000**, 51, 139-174.
- [26] M. Jeng, *American Journal of Physics*, **2000**, 68, 37-40.
- [27] A. Ceulemans, L. F. Chibotaru, S. A. Bovin, and P. W. Fowler, *Journal of Chemical Physics*, **2000**, 112, 4271-4278.
- [28] Ante Graovac, Dejan Plavšić, Matja Kaufman, Tomaž Pisanski, and Edward C. Kirby, *J. Chem. Phys.* **2000**, 113, 1925-1931.
- [29] E. C. Kirby, *J. Math. Chem.* **1990**, 4, 31-46.
- [30] E. C. Kirby, *J. Math. Chem.* **1991**, 8, 77-87.
- [31] Edward C. Kirby and Tomaž Pisanski, Paper in preparation, 2000.