

A story of silicon, soap and serendipity

DENIS WEAIRE

School of Physics, Trinity College Dublin, Dublin, Ireland

A multiple cross-fertilization of ideas between the physics of amorphous semiconductors and that of foams was helpful in both fields, in the construction of ordered and disordered network models.

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The tetrahedral bond

Conventional history points to great battles and changes of governments as its critical points. The scientist looking back on the twentieth century sees it differently, as the age when solid state physics changed the world. Few saw it coming, but we can now look back with hindsight and see how an intense focus on the properties of pure semiconductors (for whatever reason) eventually paid off. Their internal arrangement of atoms - perfectly regimented, regular and symmetric - had been first conceived for diamond carbon by Walter Nernst, in what may have been the first “ball-and-stick” crystal model [1], just before it was revealed by x-ray diffraction in 1913. Given the impact of that elegant crystal structure upon our civilisation, we may be excused for a certain obsession with perfect (or near-perfect order) for several decades.

The structure may be attributed to the nature of the Group IV atom, which lends itself to four symmetrically disposed links with other atoms, in the tetrahedral bond. In chemistry the recognition of this arrangement in molecules goes back well into the nineteenth century, when Van't Hoff's explorations of “Chemistry in Space” gave us our modern conception of the molecule as a geometrical object. His crucial insight was not immediately popular with everyone.

Kolbe's reaction was as follows:

“[...] a miserable speculative philosophy, useless in reality, while apparently deep and ingenious, is springing up like a rank growth. [...] it is again being rescued from the lumber-room of man's erratic speculations, by certain pseudo-philosophers seeking to thrust it forward surreptitiously, like some fashionably and gorgeously attired female, intruding into good society which is not her place.” [*Zeichen der Zeit, II. Journal fur Prakt. Chemie*]

The unwelcome intrusion has stayed with us ever since. However important may be the more elusive description of quantum mechanics, chemistry and much of physics remains concerned with how simple basic units can be fitted together.

As a rigid unit for building a crystal structure the tetrahedral bond leaves hardly any option than that chosen

by Nernst. But suppose we make it somewhat flexible, as chemical bonds surely are: what then?

The answer is given in nature by silicon, by germanium, by silica, even by ice (most of whose structures are essentially tetrahedral): there is a great variety of alternatives to be found in their phase diagrams. Ice has so many that Kurt Vonnegut Jr even wrote a novel based on the idea that a new one, with rather disastrous properties. In particular, all these substances can form special structures in which the tetrahedral bonds form interlocked *cages*: these are the clathrate structures.

Given this flexibility, tetrahedral bonds can even form *disordered* structures, random networks of bonds. As the work of Grigorovici, Mott and others stimulated interest in a different kind of solid state in the 1970's - that of the amorphous semiconductor - this random network structure became its prototype. Many preferred to insist that such materials were microcrystals, but they generally seem to have lost the argument, or seen it dissolve before their eyes as the microcrystals were made ever smaller in their models. For the rest of us, the random network seemed too beautiful a concept not to be found in nature.

Building random networks

Much of my own early involvement with amorphous semiconductors lay in building random networks by hand, with plastic model bonding units that some of my chemical friends still use (Fig. 1).

We worked with a combination of hand building and refinement by computer that is antiquated from today's perspective. Arguably it imparted a “feel” for the problem that the powerful direct computer methods of today cannot. Nevertheless hand-building, however enjoyable, clearly had little future. Accordingly I conceived an algorithm for creating random networks efficiently by computer [2]. Unfortunately it came to be called the WWW model (after its authors), and is now easily confused with a more celebrated network.



Fig. 1. The old fashioned approach to building model structures with tetrahedral bonds.

The method was based on a single type of local rearrangement (of a kind that had become familiar in playing with the plastic units). It was used in a simulated annealing procedure to produce a low energy disordered structure. Fred Wooten refined it and used the supercomputers of Livermore to produce lots of such structures. We called the model “Sillium” [3] by analogy with jellium, to indicate that it was an highly idealised substance, but nevertheless physically relevant. Despite this escape clause, it produced useful structures, and it seems that it remains the best way of obtaining low energy model structures for a-Si. More realistic procedures get stuck in higher energy structures. An example of a large model of the WWW type is shown in Fig. 2.

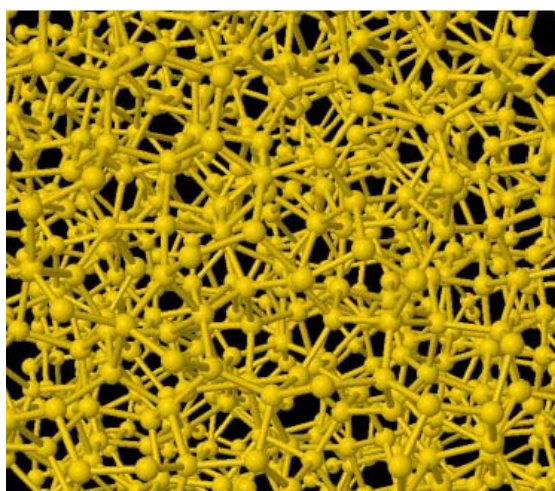


Fig. 2. A large random network model of a-Si, courtesy of N Mousseau.

I am grateful to Norman Mousseau for this, and also the gift of the latest Schick razor: the FX Diamond, which (it is claimed) shaves closer because it is coated with amorphous diamond.

Inspiration from soap

The WWW algorithm occurred to me because of work I had begun in a parallel research project. A colleague at Yale had pointed me to a paper in the library, suggesting that my obsession with the geometrical and statistical properties of amorphous silicon might find another outlet in the random structure of a liquid foam.

It was a strange paper, written from a private address in London by David Aboav, who had been a technical assistant to Eduardo Andrade in London. My friend was right: my curiosity was aroused, and I embarked on a journey into the heart of foam structures that has not yet ended [4].

Both in the interpretation of observed structural changes in foam and in building computer models for their simulation, a prominent role is played by elementary topological changes, local rearrangements of the structure. This was as first emphasised by Cyril Stanley Smith in the 1950's. His work had to do with 2D foams, as did the paper in the Yale Library which followed his lead. So The WWW model reshuffles atoms/bonds in much the same way as bubbles/lines are reshuffled in the changes that take place in the 2D soap froth.

But in terms of the structure itself, it is the 3D soap froth that comes closest in analogy to the covalent semiconductor. A sufficiently dry 3D foam consists of lines (Plateau borders) where films intersect. They form a network in which come together only in tetrahedral junctions (Fig. 3). It is a network of tetrahedral bonds. It is however a network of a more restricted kind than the covalent network: the lines enclose faces which in turn enclose cells that fill all space: these are the bubbles. In that sense, it is a *cellular* network.

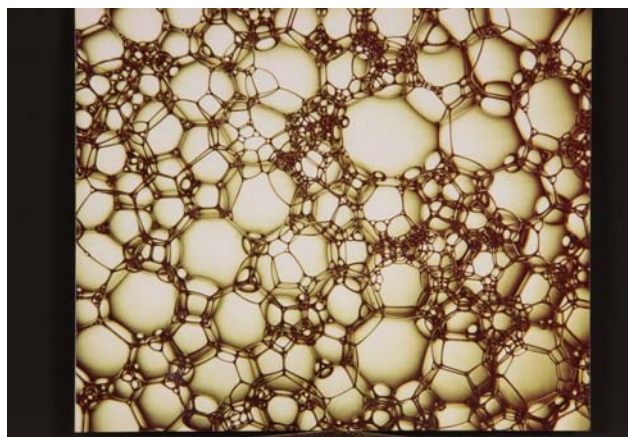


Fig. 3. An image of foam from photographer-artist M Boran.

In 1873 Joseph Antoine Ferdinand Plateau published the bible of the detailed geometry of soap froths [5]. It was he who showed experimentally and (with a little help from his friends) mathematically, that the Plateau border junctions must be tetrahedral.

He needed help from his wife and others in those celebrated experiments as well: for Plateau was blind, having destroyed his eyesight by staring at the sun in an optical experiment. The tale of his subsequent perseverance is one of the most heroic in the history of science.

The Kelvin Problem

In 1887 Lord Kelvin used Plateau's book to try to answer a question that had occurred to him in the course of a lifelong quest for a material structure of the ether of space.

Suppose (as he did at the time) that the ether is a foam of equal-sized bubbles: what structure should it have, that is, what structure has minimum energy? Energy here just means area: the total surface area of all the films that make up the bubbles.

Plateau's findings place strong constraints on what that structure could be, and Kelvin arrived quickly at a precise conjecture [6] – his foam was to be a body-centred cubic structure of identical cells which he called *tetrakaidecahedra*. He had posed the problem in September and developed all the mathematics of his solution within about six weeks – it was already published in December. This is impressive (even if we are aware that he happened to be the editor of the journal). It is an example of the energy and expedition with which he published over 650 papers, not to mention his other extraordinary achievements.

After quite a few years of analysing the two-dimensional foams which were the subject of that paper in the library in Yale, I decided it was time to go on to three dimensions, largely because computer simulations had reached that point. A new student, Robert Phelan, was duly asked to use the available software to explore some rival structures to that of Kelvin, that is, ordered but more complicated structures. But where to begin?

There was a certain amount of vague mathematical argument to the effect that five-fold rings were a desirable feature. I remembered that silicon and germanium, together with silica and ice, all formed such structures which consisted mostly of fivefold rings, forming cages. These are the *clathrates* that I mentioned earlier. Take the simplest of these. Turn it into a foam structure, in which each cage becomes a bubble (because the network is cellular, as defined above), and adjust it to minimise its energy. How does the foam structure compare with that of Kelvin?

Robert reported very quickly that it had a lower energy – that after a century of speculation and discussion of the possibility of an improvement on Kelvin's conjecture, we appeared to have found one rather easily, thanks to the analogy with semiconductor structures.

We duly sent it off to the same journal as Lord Kelvin, and published it almost as quickly.

The structure itself is a beautiful thing (Fig. 4) with delicately curved surfaces. Even if these are approximated by flat faces, it still looks good – so Robert and I published a short note with a design for a building complex, and from time to time we have suggested it to architects,

without exciting much interest. It would be something of a Buckminster-Fulleresque construction, but less symmetric than Bucky's domes: it owes its beauty to what Bacon called some "strangeness in the proportion". We have made a sculpture based on this design (Fig. 5) and a small copy is now in the collection of the Science Museum, South Kensington, London.

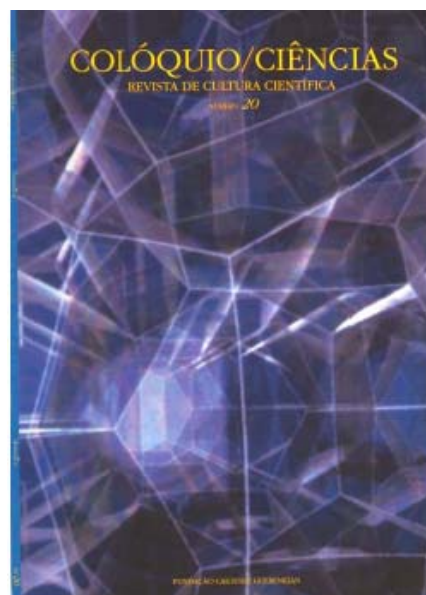


Fig. 4. A representation of the Weaire-Phelan structure, on the cover of a Portuguese magazine. Courtesy of John Sullivan.

Bubbles in Beijing

The structure has found another and much grander representation in architecture, in the design of the Water Cube, the aquatic centre for the 2008 Olympic Games in Beijing. An engineer for the Arup Corporation conceived a massive structural framework based on it (Fig. 5), adopting it as emblematic of bubbles and hence water. We await its completion in 2007.

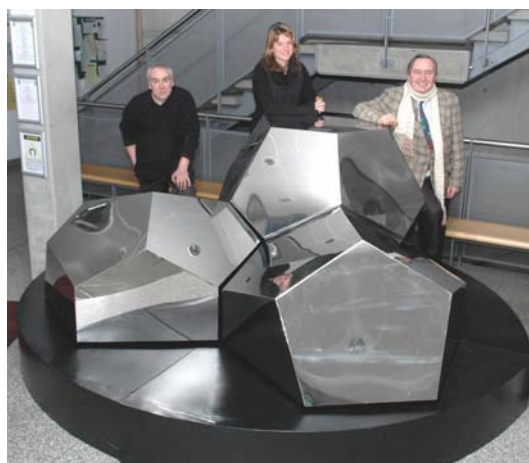
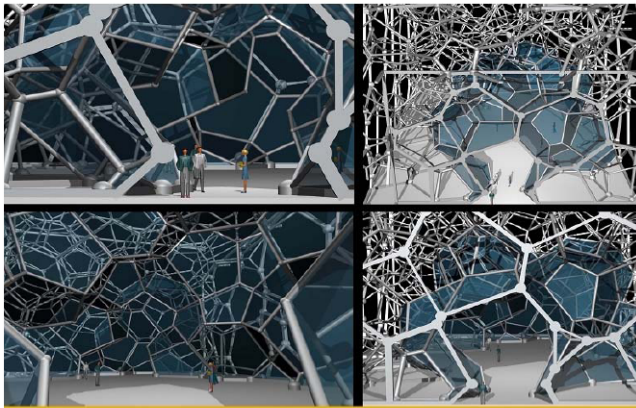


Fig. 5. A stainless steel sculpture based on the WP structure.



Beijing National Swimming Centre

Tristram Carræe

*Fig. 6. Artist's conception of parts of the Water Cube.
Courtesy of Arup Corporation.*

Although not disordered it is complex enough to carry a hint of the disorder of the ordinary foam that you find in your bath or your beer, or in the wake of an Olympic swimmer.

Conclusion

A tale as rambling as this must have a moral in the end. Surely it is that lively research is necessarily eclectic: it is often unpredictable in the connections that it makes between apparently disconnected subjects. Universities, in particular, must treasure diversity, rather than concentrate exclusively on tightly focussed research that is dictated by

fashion - or by economics, which is an even less predictable branch of science than condensed matter physics.

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*Corresponding author: dweaire@tcd.ie
denis.weaire@tcd.ie