Mixing Materials and Mathematics*

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"Oil and water don't mix" says the old saw. But a variety of immiscible liquids, in the presence of a soap or some other surfactant, can self-assemble into a rich variety of regular mesophases. Characterized by their "inter-material dividing surfaces"—where the different substances touch— these structures also occur in microphase-separated block copolymers. The understanding of the interface is key to prediction of material properties, but at present the relationship between the curvature of the dividing surfaces and the relevant molecular and macromolecular physics is not well understood. Moreover, there is only a partial theoretical understanding of the range of possible periodic surfaces that might occur as interfaces. Here, differential geometry, the mathematics of curved surfaces and their generalizations, is playing an important role in the experimental physics of materials. "Curved surfaces and chemical structures," a recent issue of the Philosophical Transactions of the Royal Society of London [1] provides a good sample of current work.

In one article called "A cubic Archimedean screw," [2] the physicist Veit Elser constructs a *triply periodic surface with cubic symmetry.* (This means that a unit translation in any one of the three coordinate directions moves the surface onto itself.) See Figure 1. The singularities of the surface are

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[1]Phil. Trans. R. Soc. London A (1996) **354**, J.Klinowski and A. L. MacKay, editors.

[2]Phil. Trans. R. Soc. London A (1996) **354** 2071-2075

dictated by: “the O^8-rod packing, well known in the study of blue phases.”[3] Motivated by investigations in materials science, Elser constructs his surface with three other properties in mind: handedness or chirality [4]; Archimedean-screw-like behavior; minimality.

The model surface with these properties is the *helicoid*—the surface swept out by a horizontal line rotating at a constant rate as it moves at constant speed up a vertical axis. (See Figure 2.) It divides space into two congruent regions[5]and we can take the helicoid to be the boundary of either one of them. It is evident that a vertical translation has the same effect on the helicoid as a proportional rotation about the vertical axis. (In particular, translate enough to make one full rotation and you are back to the original surface. This shows that the helicoid is *singly periodic*.)

Put a helicoid inside a vertical cylinder filled with fluid and you have an Archimedean screw, a rotation of which translates the fluid up or down. Which way the fluid is pushed is a function of which way the generating line of the helicoid turns around the axis; helicoids have handedness. And the helicoid is a *minimal surface*, a property whose importance for materials science will be described below.

First, to understand what it means for a surface to be minimal, do the following thought-experiment. Imagine the surface sculpted from a thin rigid material. Cut out a small piece, save it, and then form a soap film over the hole. The shape of the film is determined by the boundary of the hole and the physical behavior of the soap film; it tries to minimize its area. If the soap film matches the piece you saved, and if this works everywhere you try it, the surface is minimal. A geometer would condense this by defining a minimal surface as one that is “locally area-minimizing.” An engineer might think of a minimal surface as a membrane interface between two gases at the same pressure, which by the Laplace-Young law will have zero mean curvature (another way to characterize minimality).

Why do such surfaces occur in compound materials? Reducing surface area between two materials that are naturally repelling will reduce the total energy. It is therefore plausible that, to first order at least, the interface should be a minimal surface. [6] Since this is happening in the same

[3]Elser, op. cit. See also B.Pansu and E. Dubois-Violette, Blue Phases: Experimental survey and geometric approach in *J. Phys. Colloq.***57** C7-281 (1990).

[4]An object is chiral if it is not identical to its mirror image.

[5]Two regions are congruent if they can be made identical by a rigid motion.

[6]When there are unequal volume fractions or a there is a nonzero pressure differential across the membrane, the resulting surface will have nonzero constant mean curvature.

way everywhere in the substance, it is also reasonable to expect that, at a supramolecular length scale, the structure should be homogeneous, i.e. the interface should be periodic.

How would you recognize a periodic, space-dividing minimal surface if you happened to run into one? The helicoid was identified as a minimal surface in 1776, but the first doubly periodic example was not discovered until the 1830's by H. Scherk [7] and the first triply periodic example was found only some 35 years later by H. Schwarz. More examples were found around the turn of the Century, but the subject slowly receded below the mathematical horizon. In fact, periodic minimal surfaces have gone in and out of mathematical fashion for the last 150 years.

The latest revival dates to the late 1960s when A. Schoen, then working for NASA and interested in strong-but-light structures, found several new triply periodic, space-dividing minimal surfaces.[8]For many years these surfaces were better known among materials scientists than among mathematicians. Since the early 1980s, they have been again of interest to differential geometers, in part due to their importance in materials science. Recognizing minimal surfaces is much easier now that computer simulation and graphics are widely available. [9]

Schoen's most spectacular discovery was the the *gyroid,* pictured in Figure 3a below. After 30 years of obscurity, it is currently the darling of researchers who study block copolymers. Claims have been made that this surface and its companion constant-mean-curvature surfaces are found in many materials.[10]

To simplify calculations, materials scientists and crystallographers have substituted for the gyroid— and for most other triply periodic minimal surfaces—the locus of solutions to a single equation involving trigonometric

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The archetypical example of such a surface is a sphere.

[7]See also NATURE **334** N.6183, Aug. 18,1988 598-601 for a description of Scherk's surface and for examples of periodic minimal surfaces found as inter-material dividing surfaces in block copolymers.

[8]A. Schoen, Infinite periodic minimal surfaces without self-intersections. NASA Technical Note TN D-5541(1970). See also S. Hildebrandt and A. Tromba, The parsimonious universe: shape and form in the natural world. Copernicus(Springer Verlag) N.Y. 1996 197-202

[9]These changes are reflected in some of the other articles in "Curvature and chemical structure,"most clearly in Karcher, H. and Polthier, K. Construction of triply periodic surfaces, Phil. Trans. R. Soc. London A (1996) **354** 2077-2104

[10]See, e.g., Hajduk et al. Macromolecules, **27**, 4063-4075 (1994)

functions in three space variables. For example, the solution to

$$\sin x \cos y + \sin y \cos z + \sin z \cos x = 0$$

is, visually, amazingly close to the gyroid. (See Figure 3b.) The utility of studying such "zero-set surfaces" for material-science purposes is explored in detail in another article in this same issue. [11] Among other things, by looking at level-set surfaces with zero replaced by a small value, they allow rough approximation of families of interface candididates whose mean curvature is expected to be close to constant, and which divide space into regions of unequal volume per unit cell.

These functions are not found by chance; they come either from choosing an appropriate low-order term from the Fourier series of an electrostatic potential function derived from charges whose distribution has the desired space-group symmetry, or from a symmetrization procedure using generators of the space group. But there is as yet no real explanation as to why the match is so good in some cases and not at all accurate in others. From a mathematical point of view there are other problems with this approach. For one thing, these zero-set surfaces are not minimal surfaces, yet are often treated as such in the materials science literature. Properties of minimal surfaces are claimed for them when convenient; when not convenient or when they contradict experiment, these same properties are simply ignored.

Elser's surface is a zero-set surface. (Actually, it is the union of three copies of a zero-set surface. They meet along the network of lines illustrated in Figure 1.) It is not minimal (he acknowledges it) and it is not known whether or not there is a minimal surface close to it in the sense that the gyroid is close to the zero set of the equation above. Moreover, the conversion of a rotational motion to a translation, the Archimedean-screw property, is not a property of this surface at all, but a property of a *family* of zero-set surfaces, considered as a deformation of the original one. None of them are minimal and no two of them are congruent. They are not even locally isometric and only exhibit a weak form of handedness when taken as a family.

For a mathematician this is troublesome. Consider that the gyroid was only recently shown by rigorous mathematical means to be a space-dividing surface.[12] For geometers, this is an important, if not earth-shaking, result even though the evidence for its validity is overwhelming from carefully generated computer images. For geometers, simulating a surface on a computer

[11] C. Lambert,L. Radzilowski, E. Thomas, Level surfaces for cubic tricontinuous block copolymer morphologies. Phil.Trans. R. Soc. London A (1996) **354** 2009-2024.

[12] K. Grosse-Braukmann and M. Wohlgemuth SFB 256 Preprint, U. Bonn (1995)

is a step along the way to understanding it mathematically, while a materials scientist has no use for an abstract surface without the ability to visualize it. The mathematicians H. Karcher and K. Polthier , in their article in the same issue of the Phil. Trans., express this huge difference in professional methodology by observing that *"So far, outside mathematics, only pictured minimal surfaces have been accepted as existing. In such cases one can see whether they have self-intersection. In mathematics, we look for theorems that prove there are no self-intersections."* [13]

Yet it is impossible to deny that pictures of Elser's surfaces may be useful in the understanding of blue phases in liquid crystals. As a mathematician, I struggle to appreciate this while at the same time I recoil at seeing important distinctions—and sometimes basic definitions—misused or ignored.

Archimedes had something relevant to say about this situation. Discussing the difference in mathematics between means of discovery and methods of proof, he wrote: *"…certain things became clear to me by a mechanical method, although they had to be demonstrated by geometry afterward because their investigation by the said method did not furnish an actual demonstration. But it is of course easier, when we have previously acquired, by the method, some knowledge of the questions, to supply the proof than it is to find it without any previous knowledge…"*[14]

In thought-experiments and in real ones, Archimedes applied mechanics, the law of the lever in particular, to discover geometric relationships He then tried to prove them by more formal means and often he succeeded. What appears to be happening in materials science today can be viewed as an inversion of this process. Namely, physical structures are being discovered by the sometimes very loose application of differential geometry. Their validation depends on whether these structures organize and predict observable phenomena, not on whether or not the theory was used correctly from a mathematical standpoint.

Materials science and mathematics may be immiscible, but with computer simulations and computer graphics as surfactant, there are interacting in unusual and productive ways.

[13] op.cit. page 2081

[14] On the Method, Introduction,2 T. L. Heath trans. Cambridge University Press 1912, as quoted in *Greek Science in Antiquity,* by M. Clagett. Collier-Macmillan, 1966

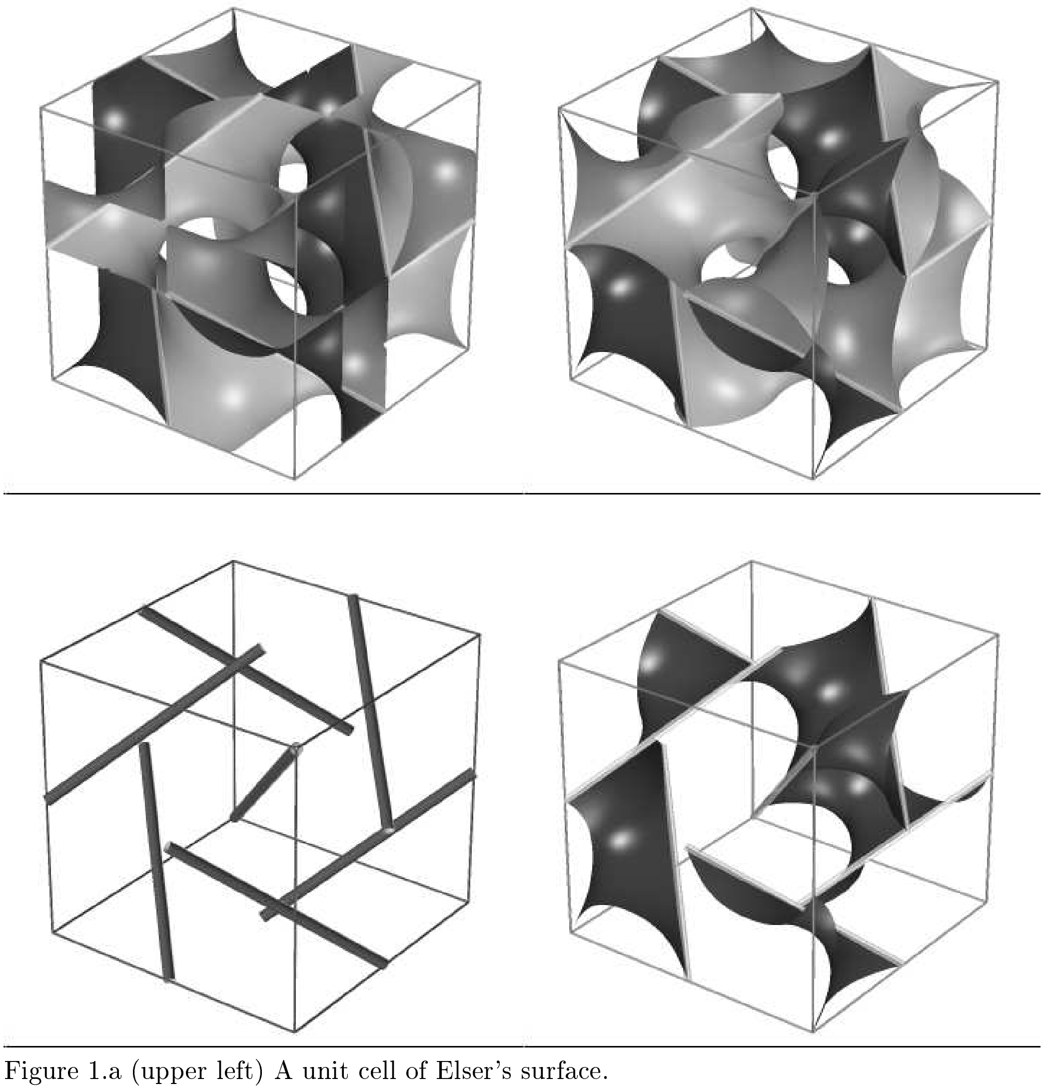

Figure 1.a (upper left) A unit cell of Elser's surface.

Figure 1.b (upper right) A unit cell of a one of the surfaces in the family. This one is in the middle of the family. An animation of the entire family is available (after Figure 3a) in an electronic version of this paper: http://www.msri.org/Computing/david/papers/nature96/

Figure 1.c (lower right) One of the three congruent surfaces that meet at 120 degree angles along the line singularities to form the surface in 1b.

Figure 1.d (lower left) Line singularities: rod packing with octahedral symmetry.

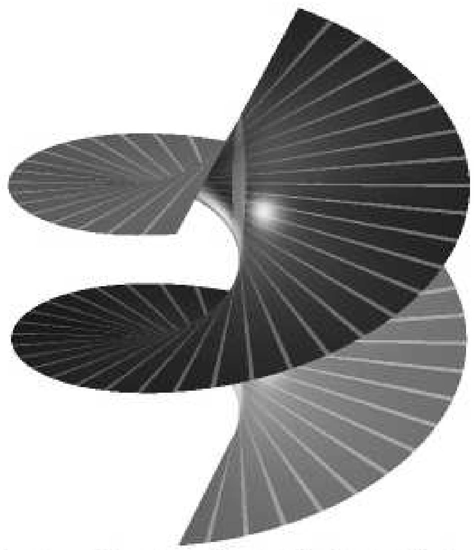

Figure 2. The Helicoid

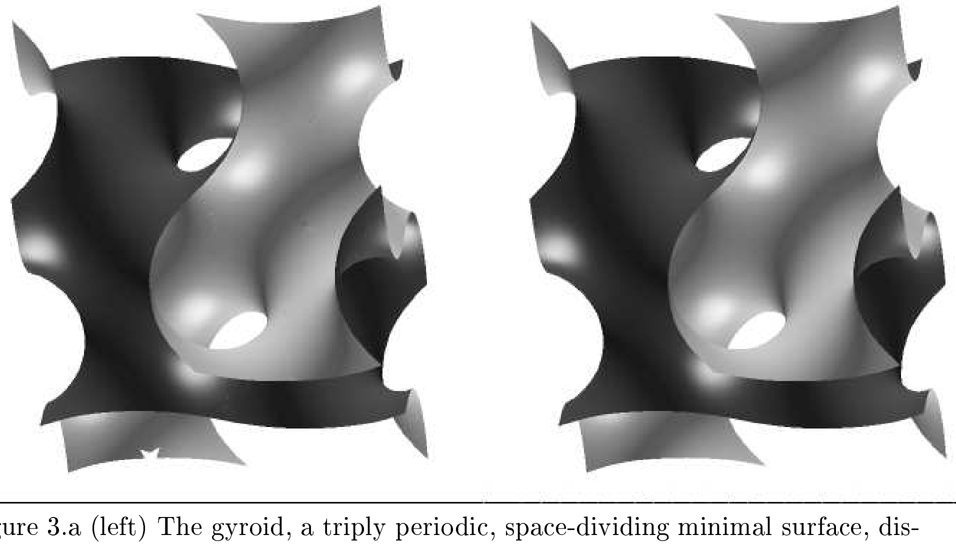

Figure 3.a (left) The gyroid, a triply periodic, space-dividing minimal surface, discovered by A. Schoen in the late '60s. It contains no lines and has no reflective symmetries. It's space group is $I4_132$.

Figure 3.b (right) The solution set to $\sin x \cos y + \sin y \cos z + \sin z \cos x = 0$