New Tetrahedrally Close-Packed Structures

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Abstract

We consider mathematical models of foams and froths, as collections of surfaces which minimize area under volume constraints. Combinatorially, because of Plateau's rules, a foam is dual to some triangulation of space. We examine the class of foams known as tetrahedrally close-packed (TCP) structures, which includes the one used by Weaire and Phelan in their counterexample to the Kelvin conjecture. In particular, we construct infinite families of new periodic TCP structures, all of which are convex combinations of the three basic TCP structures (A15, Z and C15). The construction can also be used to create TCP triangulations of three-manifolds other than Euclidean space; these are not such convex combinations.

1 Soap films and foams

Soap films, bubble clusters, and foams and froths can be modeled mathematically as collections of surfaces which minimize their surface area subject to volume constraints. Remember that a surface in space has (at each point) two *principal curvatures* k_1 and k_2. Because there is no way to globally distinguish the two, only their symmetric functions are physically meaningful. The *mean curvature* is their sum $H = k_1 + k_2$ (twice the average normal curvature).

A soap film spanning a wire boundary, with no pressure difference across it, will be a minimal surface (with $H = 0$), but in general we need to consider the effect of volume constraints in bubble clusters. With these constraints, we find that each surface has constant mean curvature $H \equiv c$, so it is called a *CMC surface*. Here the constant is the Lagrange multiplier for the volume constraint, which is exactly the pressure difference across the surface; this relation $H = \Delta p$ is known as Laplace's law.

Almgren proposed the following *bubble cluster problem*: enclose and separate regions in space with given volumes $V_1, \ldots, V_k$, using the least total area. He then proved that a minimizer exists and is a smooth surface almost everywhere [1] (see also [6]). It follows that the smooth pieces are CMC surfaces; these meet along certain singularities. Later, Taylor was able to show [14] that the singularities observed empirically in soap films by Plateau [10] are the only ones possible in a minimizing bubble cluster.

That is, such a cluster consists of a finite union of smooth surfaces, meeting in threes at 120° dihedral angles along a finite number of smooth curves; these curves in turn meet at finitely many tetrahedral corners (which look like the soap film obtained when dipping a

tetrahedral frame into soapy water—six sheets come together into the central singularity, along four triple curves).

We will define a foam mathematically as a (locally finite) collection of CMC surfaces, meeting according to Plateau's rules, and satisfying the cocycle condition: pressures can be assigned to each component of the complement so that the mean curvature of each interface is the pressure difference. We will call the components of the complement the *cells* of the foam, call the interfaces between them simply the *faces*, call the triple junction lines where they meet the (Plateau) *borders*, and call the tetrahedral singularities the *corners*.

2 Combinatorics of foams

For many purposes, we can ignore the geometric parts of Plateau's rules, and only pay attention to the combinatorics of the foam's cell complex. The combinatorial rules mean that the *dual cell complex* to a foam is in fact a simplicial complex, that is, a triangulation of space. To construct this dual, we put a *vertex* in each cell of the foam. Vertices in a pair of adjacent cells are connected by an *edge*, which is dual to a face of the foam. Where three faces come together along a border, we span the three corresponding edges with a *triangle*; and where four borders come together at a corner, we fill in a *tetrahedron*.

Combinatorially, the Plateau rules mean that a foam and its dual triangulation are like a Voronoi decomposition of space and the dual Delone triangulation. Given a set of *sites* in space, the Voronoi cell [7, 11] for each site is the convex polyhedron consisting of points in space closer to that site than to any other. If the sites are in general position (with no five on a common sphere) then the dual Delone complex (whose vertices are the original sites) is completely triangulated; each Delone tetrahedron has the property that no other sites are inside its circumsphere.

This similarity suggests that we might look for foams as relaxations of Voronoi decompositions. For instance, we can give a modern interpretation to Kelvin's construction [15] of his candidate for a least-area partition of space into equal volume cells as follows: Start with sites in the body-centered cubic (BCC) lattice. Their Voronoi cells are truncated octahedra, packed to fill space. If we let the films in this packing relax (until the geometric parts as well as the combinatorial parts of Plateau's rules are satisfied) we should get a periodic foam, the one proposed by Kelvin.

Now consider a triangulation of any compact three-dimensional manifold, and let V, E, F and T be the numbers of vertices, edges, triangles and tetrahedra, respectively. Let z be the average number of edges at a vertex (which is the average number of faces on a cell of the dual foam), and n be the average valence of an edge (the average degree—or number of borders—of a face in the foam). Then a multiple-counting argument shows that

$$4T = 2F, \qquad 3F = nE, \qquad 2E = zV.$$

But since the Euler characteristic of any compact 3-manifold is zero, we have $0 = \chi = V - E + F - T$. Combining these results gives

$$6 - n = 12/z,$$

which again is valid for any triangulation of any three-manifold, independent of topology.

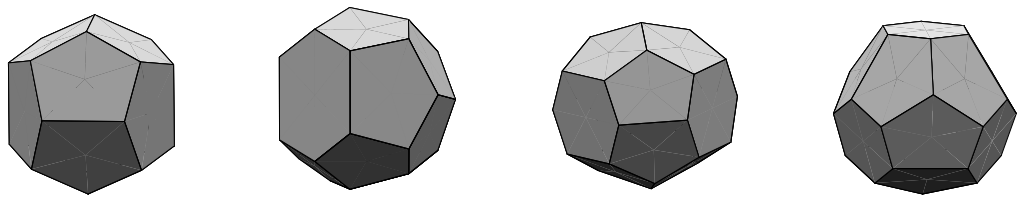

Figure 1: There are four types of cells found in TCP foams, each with 12 pentagonal faces like the dodecahedron at the left. The remaining three have in addition two, three or four hexagonal faces, arranged antipodally, equatorially, and tetrahedrally.

Of course, a regular Euclidean tetrahedron cannot tile flat space; its dihedral angle is $\arccos\frac{1}{3} \approx 70.53°$, so we would need

$$n = n_0 := \frac{2\pi}{\arccos\frac{1}{3}} \approx 5.1043, \quad z = z_0 := 12/(6 - n_0) \approx 13.397$$

in such a tiling. This value z_0 is also 4π divided by the measure of the solid angle at the vertex of a regular tetrahedron.

If we view average dihedral angle as a function on the space of tetrahedra, by symmetry it has a critical point at the regular tetrahedron (as the Shoemakers [12] have pointed out—see below). Thus, if we tile Euclidean space by nearly regular tetrahedra, we expect the average dihedral angle to be very close to $\arccos\frac{1}{3}$. But the geometric part of Plateau's rules says that each corner in a foam has exactly tetrahedral angles. So, if the borders in the foam are not too curved, the dual triangulation should consist of nearly regular tetrahedra. Thus we expect $n \approx n_0$ for such a foam.

3 TCP structures

The tetrahedral angle $\arccos(\frac{-1}{3}) \approx 109.47°$, found at foam corners, is of course intermediate between the average angle of a pentagon (108°) and that of a hexagon (120°). We are led to consider foams with only pentagonal or hexagonal faces.

Chemists have studied transition metal alloys in which the atoms pack in nearly regular tetrahedra. These tetrahedrally close-packed (TCP) structures were first described by Frank and Kasper [2, 3], and have been studied extensively by the Shoemakers [12] among others. In all of these structures, the Voronoi cell of each atom has one of four combinatorial types; these are exactly the four polyhedra which have only pentagonal and hexagonal faces, with no adjacent hexagons. Mathematically, we can define TCP structures in this way [4]: triangulations whose combinatorial duals (called TCP foams) have only these four types of cells. Since this definition deals only with the combinatorics of the triangulation, presumably it allows some examples with too much geometric distortion to work chemically as TCP structures.

Each of the four types of cells found in TCP foams has 12 pentagonal faces, as seen in Fig. 1. One type is the (pentagonal) dodecahedron. Cells of the other three types have additionally two, three, or four hexagonal faces, which are arranged antipodally, equatorially, or tetrahedrally (respectively). The 14-hedron can be viewed as a "$\frac{6}{5}$-fold unwrapping" of a dodecahedron, since it has six-fold symmetry through the centers of the opposite hexagons.

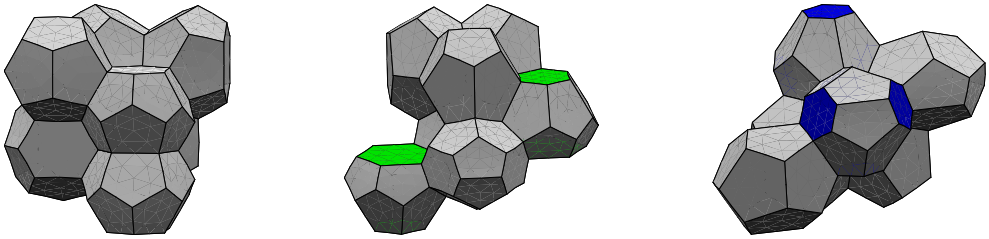

Figure 2: The three basic TCP structures. A15, left, has two 12-hedra (one upper-left) and six 14-hedra (in colums like lower right) in a cubic cell. Z, center, has three 12s (top), two 14s (in vertical columns but separated in the figure, with unequal horizontal hexagons), and two 15s (with vertical hexagons, one lower front). C15, right, has four 12s and two 16s (with hexagons darkened) in a cubic cell.

Perhaps some geometric condition on the tetrahedra (saying that their edge lengths or dihedral angles are close to equal) would guarantee that the dual cells could only be one of the four TCP types. Note however, that edge lengths differ less in BCC tetrahedra (where they are 2 and $\sqrt{3}$) than in the TCP structure A15 (where they are 2, $\sqrt{5}$ and $\sqrt{6}$).

It is an interesting open question just what foams are possible with these four types of cells. Dually, we are asking for triangulations of space in which each edge has valence five or six, and no triangle has two edges of valence six. We know we cannot use only dodecahedra, since a foam made of these alone (meeting tetrahedrally) will fill a spherical space, not $\mathbb{R}^3$.

This seems to be the only mathematical theorem restricting how these cells can fit together, but the chemists have made interesting additional observations. We can define three *basic* periodic TCP structures. A15, observed for instance in Cr_3Si, has one 12-hedron and three 14-hedra in a fundamental domain. Z, observed in Zr_4Al_3, has three 12-hedra, two 14-hedra, and two 15-hedra. And C15, observed by Friauf and Laves in $MgCu_2$, has two 12-hedra and one 16-hedron. (These are shown in Fig. 2 and described in more detail below.)

If we describe potential TCP structures by the ratio of cells they have of the four types, we could plot them all within an abstract tetrahedron, as convex combinations of the four vertices. But the observation of Yarmolyuk and Kripyakevich [18] is that all known TCP structures are, in fact, convex combinations of the three basic ones just mentioned, so they all get plotted within the triangle of Fig. 3. As we mentioned before, the Shoemakers [12] attempt to explain this observation by noting that even for a tiling by tetrahedra somewhat distorted from regular, we expect to have $z \approx z_0$. Certainly the three basic TCP structures, with $z = 13\frac{1}{2}$ for A15, $z = 13\frac{3}{7}$ for Z, and $z = 13\frac{1}{3}$ for C15, are close to this value. We will describe below how to construct some new convex combinations of these basic structures; the resulting foams will of course also have $z \approx z_0$.

It is interesting to note that there are other chemical structures, clathrates and zeolites, which exhibit the structure of the TCP Voronoi cells (that is, the dual TCP foams) more explicitly, with atoms at the foam corners. For more details, see O'Keeffe [8], or the discussion in [13].

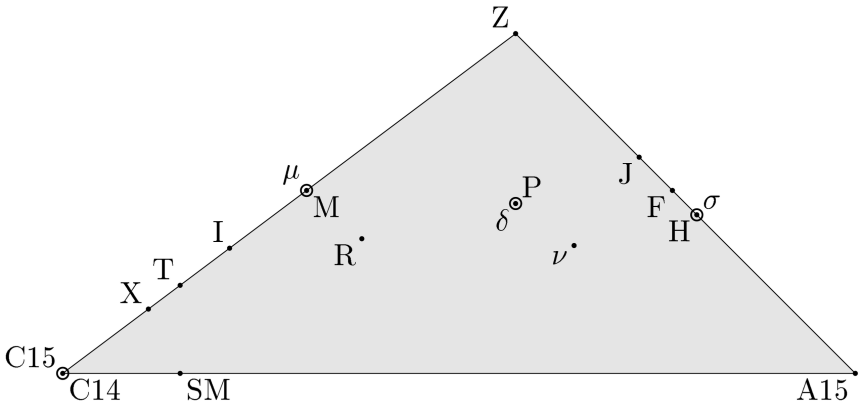

Figure 3: The basic TCP structures A15, Z, and C15 lie at the corners of this triangle, where the horizontal axis plots the average number of faces per cell (ranging from $13\frac{1}{3}$ to $13\frac{1}{2}$) and the vertical axis plots the fraction of cells which are 15-hedra (ranging from 0 to $\frac{2}{7}$). Every known TCP structure, when described by its numbers of 12-, 14-, 15-, and 16-sided cells, is a convex combination of these three. Distinct structures may appear at the same point.

4 Some constructions for TCP foams

Perhaps the most common partition of space into equal-volume cells is by cubes, which form the Voronoi cells for the simple cubic lattice. Of course this is a degenerate case of the Voronoi construction, and the cells fail to meet tetrahedrally, so this does not make a good foam. These degenerate cubic corners (at the "holes" in the lattice) themselves form another cubic lattice. The two taken together form the BCC lattice. This lattice, of course is the one whose Voronoi cells give rise to the Kelvin foam.

We might consider now repeating the process, adding some holes as new sites. The BCC lattice has only one kind of Voronoi corner (or hole). If the lattice is scaled so neighboring sites are at distance 4 and $2\sqrt{3}$ then the corner is at a distance of $\sqrt{5}$ from the nearest sites. Adjacent corners are much closer to each other, at distance $\sqrt{2}$, so if we added them all as sites, we would not be close to having regular Delone tetrahedra. But because all the faces in the foam have even numbers of sides (4 or 6), these corners can be colored black and white so that adjacent corners are different colors. If we look now just at black corners, adjacent ones are at distance 2 or $\sqrt{6}$. The structure with Si atoms at the BCC lattice points, and Cr atoms at these black corners, is the A15 structure of Cr_3Si. Its Voronoi decomposition has cells of two types (12- and 14-hedra) and forms the TCP foam of Weaire and Phelan [17], corresponding to a Type I clathrate.

If we start with the face-centered cubic lattice, it has rhombic dodecahedra for its Voronoi cells. The corners include the deep holes and (up to lattice translation) two kinds of shallow holes. The original lattice together with one kind of shallow hole forms the diamond network. If we take all its points as sites and repeat the Voronoi construction, the new corners include all the other original holes, plus certain new holes. The C15 structure for $MgCu_2$ has Mg atoms in the diamond network and Cu atoms at these new holes. Its Voronoi diagram in turn is the C15 foam, corresponding to a Type II clathrate. We could construct Z in a similar fashion, filling in certain holes in a lattice of hexagonal prisms.

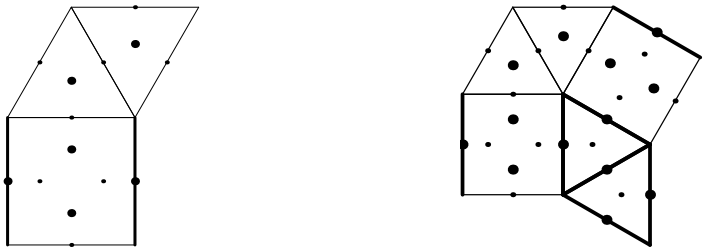

Figure 4: Here are two examples (σ, left, and H, right) of the construction for TCP structures from tilings by squares and triangles. In each case we see only a fundamental domain. The thick and thin lines correspond to the red and blue edges in the text. Small dots are sites at height $4k+1$, large dots are sites at height $4k-1$, and the square and triangle vertices have sites at height $2k$.

The work of the Frank and Kasper suggests the following construction for infinitely many new TCP structures, as convex combinations of A15 and Z. Consider an arbitrary tiling of the plane by squares and equilateral triangles. (The regular square 4^2 and triangular 3^6 tilings will give A15 and Z, respectively.) We will describe the location of sites in space for a corresponding TCP structure. Over each vertex we will find a vertical stack of 14-hedral cells, sharing hexagons, and centered at even integer heights.

Each edge of the tiling makes an angle some multiple of 30° with the horizontal. We mark it red or blue depending on whether this is an odd or even multiple, as in Fig. 4. The edge colors are the same around any triangle, but alternate around a square. At odd heights we find two different kinds of layers, with centers of 12-, 14-, and 15-hedral cells. The layers at height $4k+1$ have sites at the midpoints of the blue edges, at the centers of the red triangles, and also halfway between the center of any square and each of its red edges. The layers at height $4k-1$ are constructed in the same fashion, after interchanging red and blue.

There are infinitely many possibilities here; if the tiling we start with has triangles and squares in the ratio $2a : b$, then the foam obtained has 12-, 14- and 15-hedral cells in the ratio $3a+2b : 2a+6b : 2a$, which is just the appropriate convex combination of the ratios for Z and A15. Periodic tilings lead to periodic structures; the simplest ones have been observed in nature as TCP structures. For instance, the semi-regular tiling with vertices 3^34^2 (which alternates layers of squares and triangles) gives the H structure, while the one with vertices 3^2434 (the snub square tiling) gives the σ structure.

We can extend this construction much more generally, in a way that also encompasses arbitrary combinations of Z and C15, and furthermore allows TCP tilings of any three-manifold $\Sigma^2 \times S^1$. We will describe this extension only combinatorially, without putting any constraints on particular geometry.

For this, let Σ be any surface, and consider an arbitrary tiling of Σ by triangles and squares (more properly, quadrilaterals). Also mark certain of the edges in this tiling green, but with no two adjacent green edges around any tile. In the three-manifold $\Sigma \times S^1$, we will think of S^1 having height four, and as before, at even heights we will places sites above the vertices of our tiling. At the two different odd heights, we will again place sites either at midpoints of the tiling edges or within the tiles (one in a triangle or four in a square, as before). But now, we omit midpoints of any green edges; instead, across a green edge, we switch the two odd layers.

A tile vertex incident to T triangles, S squares, and G green edges will become a site of valence $2T+3S-G+2 = 12+W$ in three dimensions; we want this to be 12 or 14, that is, $W = 0$ or 2. Note also that, if the tiles were regular polygons, $2-W-G = 12-(2T+3S)$ would be the angle defect at the vertex (measured in units of 30°).

There are only twenty possibilities of combinatorial types of vertices in this tiling. When $W = 2$, we have $G = 0$ with type 3^6, 3^34^2 or 4^4, or $G = 1$ with one square replacing a triangle (3^54 or 3^24^3), or $G = 2$ with one extra triangle (3^7, 3^44^2 or 34^4), or $G = 3$ with one extra square (3^64 or 3^34^3), or finally $G = 4$ with type 3^8. When $W = 0$, we have exactly the same list of types, each with one fewer triangle (except that $G = 4$ is impossible). Note that $G + S$ is always even; this means that the role of the two odd layers is locally consistent around each vertex.

Let v be the number of vertices with $W = 0$ and w the number with $W = 2$, s and t are the numbers of squares and triangles, and g and e the numbers of green and other edges. Furthermore, let s_i and t_i denote the number of squares or triangles with exactly i green edges. If we sum over all vertices, we get

$$\sum T = 3t, \quad \sum S = 4s, \quad \sum G = 2g, \quad \sum W = 2w, \quad \sum(2 - W) = 2v.$$

Also, we have

$$s = s_0 + s_1 + s_2, \quad t = t_0 + t_1, \quad 4s + 3t = 2(e + g), \quad t_1 + s_1 + 2s_2 = 2g.$$

Furthermore, if χ is the Euler characteristic of Σ, we find

$$(v + w) - (g + e) + (s + t) = \chi = (v - g)/6,$$

where the latter equation comes from summing the angle defects and using Gauss-Bonnet.

The sites over edge midpoints have valence 12, as do those over vertices with $W = 0$. The sites over the other vertices have valence 14, as do those within squares (not near a green edges). Sites over triangle centers (with no green edges) have valence 15, as do those near a green edge of a square. Finally, sites over triangle centers with a green edge have valence 16. Thus if X, P, Q, R denote the numbers of sites of valence 12, 14, 15, 16, respectively, then we have

$$X = 2v + e, \quad P = 2w + 4s_0 + 3s_1 + 2s_2, \quad Q = t_0 + s_1 + 2s_2, \quad R = t_1.$$

We also find that the major skeleton of the resulting TCP structure (consisting by definition of the edges of valence six in the triangulation) includes vertical lines through all vertices with $W = 2$. The rest of the skeleton connects sites at the odd heights, passing horizontally straight through each square, horizontally across each nongreen edge, and zigzagging up and down across each green edge.

Combining this information with the Euler number relations, we find that when $\chi = 0$ (for a periodic foam in Euclidean space) the cell counts are a convex combination of those in the three basic TCP structures, as we claimed. In fact, a structure is such a convex combination iff $P \geq Q$ and $B = 0$, where

$$B := 6X - 2P - 7Q - 12R$$

measures the deviation from being such a combination.

For our structures,

$$\begin{aligned} B &= 12v + 6e - (4w + 8s_0 + 6s_1 + 4s_2 + 7t_0 + 7s_1 + 14s_2 + 12t_1) \\ &= 12v + 6e - (4w + 2(e+g) + 4(t+s) + 10g) \\ &= 16(v-g) - 4\big((v+w) - (e+g) + (t+s)\big) \\ &= 92\chi. \end{aligned}$$

Thus $B = 0$ when Σ is a torus with $\chi = 0$, meaning that all the periodic TCP structures we construct in Euclidean space are convex combinations of the basic ones. For different Σ, we see exactly how the TCP tilings we construct fail to be such convex combinations.

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