

Foams are found everywhere: in nature, in technology, in our home. They are examples of cellular materials: assemblies or clusters of cells (from Latin cella: a small compartment or enclosed region) packed together so that they fill space without gaps. Foams come in different kinds. Ordinary liquid foam is an experimental system that solves some difficult geometry problems.

FOAM

AS A GEOMETER

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* DOI: 10.1051/e pn/2009502

▲ Organic cellular abstract in blue with white background. ©iStockPhoto

If the walls bounding the cells are solid, and their contents liquids or gases, we are dealing with a *solid foam* or a *cellular solid*. These are common in nature: wood, cork, sponge and coral are examples. Mankind has made use of cellular solids for millennia, as witness artifacts retrieved from the pyramids of Egypt. More recently, we have turned to producing our own cellular solids, tailored to specific purposes. At the simplest level there are honeycomb-like materials, made up of parallel, prismatic cells, which are used for lightweight packaging and structural components. More familiar are the polymeric foams, found in everything from the humble disposable coffee cups to modern car bumpers and thermal insulation layers in buildings and refrigerated vehicles. Techniques now exist for foaming not just polymers, but also metals, ceramics and glasses.

Metal foams are finding applications as shock absorbers in the automotive industry, whereas ceramic and glass foams, because of their good biocompatibility, can be ingrown by living tissue, thereby aiding the integration of dental and bone implants coated with them [1].

On the other hand, a *liquid foam* consists of a mixture of two fluids, and yet behaves as a solid if subjected to only very small stresses. When one of the fluids is air, the cells are usually called bubbles. Typically the thickness of a wall separating two bubbles is much smaller than the linear size of a bubble, and the walls can then be idealised as curved surfaces, which meet on lines, which in turn meet in vertices. This is the limit of a perfectly dry, or mathematical, foam. In two-dimensional (2D) perfectly dry foams we have only lines (cell walls) which meet in point vertices. Real foams, by

contrast, all have a finite liquid volume fraction which can be as high as 30%; these are wet foams (see figure 1). Most of the liquid resides in the channels along which

One aims at delivering drugs in such a way that they react only after reaching some specified location

films meet, called Plateau borders; in 2D these coincide with the vertices. A real foam may be called ‘dry’ if its Plateau borders (in 2D) or Plateau borders and vertices (in 3D) are of negligible size; this corresponds to a liquid area (in 2D) or volume (in 3D) fraction of a few percent [2].

Traditional applications of liquid foams include drinks such as beer and sparkling wines; foodstuffs such as whipped cream and chocolate mousse; household cleaning products such as oven cleaner and limescale remover; and toiletries such as shaving cream. Various industrial separation processes also utilise the properties of foams. In fractionation, a solute that is adsorbed at the bubble surfaces can be removed from solution. In flotation, metal-rich, hydrophobic particles stay in the foam, while metal-poor hydrophilic ones drain out. Fire-fighting foams perform an all-out attack on the three ingredients necessary to sustain a fire: they exclude oxygen, lower the temperature, and trap fuel vapour. Finally, in enhanced oil recovery, foam acts as a surfactant carrier for flushing oil out of the interstices in reservoirs.

The behaviour of a dry foam with a low-viscosity liquid phase (e.g., an aqueous foam, as opposed to a polymeric foam) is dominated by surface tension. The films tend to contract in order to minimise their surface

area and hence their energy. This is opposed by the pressure difference across the film separating bubbles i and j , according to Laplace’s equation:

$$p_i - p_j = \gamma \left(\frac{1}{R_{ij}^{(1)}} + \frac{1}{R_{ij}^{(2)}} \right) \quad (1)$$

where γ is the film tension, $p_i(p_j)$ is the pressure inside bubble $i(j)$, and $R_{ij}^{(1)}, R_{ij}^{(2)}$ are the radii of curvature of the surface between bubbles i and j . The rules for the equilibrium of such a foam are embodied in Plateau’s laws, discovered experimentally in the second half of the 19th century [3] and later proved [4] to be necessary conditions for stability. They are:

1. Films meet three at a time, at 120°-angles, along Plateau borders.
2. No more than four Plateau borders may meet at a vertex, where the angle between any two of them is the tetrahedral angle, 109.5°.
3. Film curvatures sum to zero at a vertex (from Laplace’s law).

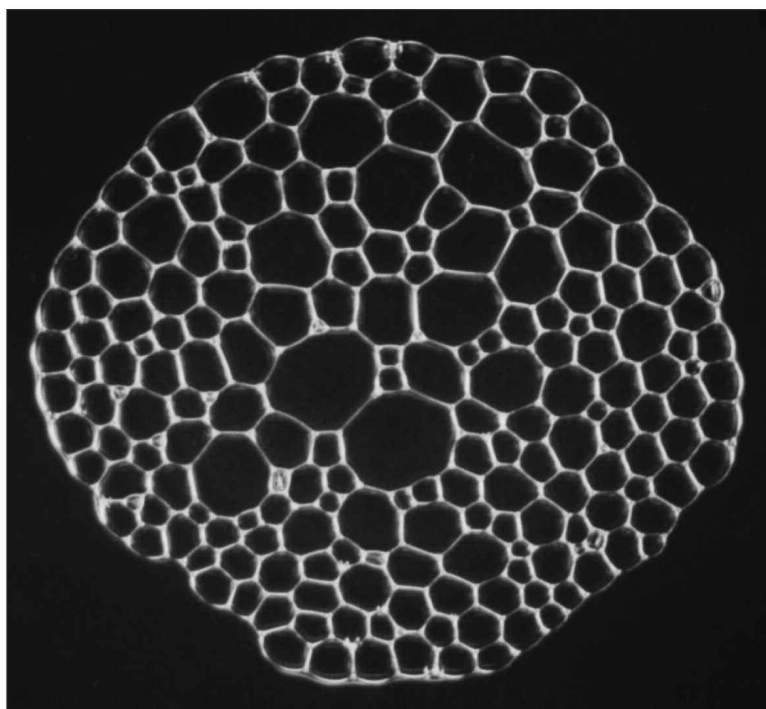
In 2D there is one additional rule (which also follows from Laplace’s law) that the films must be arcs of circle (since there is only one radius of curvature and this must be constant).

Unlike a solid foam, a liquid foam is inherently unstable and will eventually disappear, though there are recorded instances of foams surviving weeks or even months, if kept in sheltered conditions. The mechanisms for foam instability are three:

- **Drainage:** under gravity, liquid will drain out until an equilibrium state is reached. This occurs on a timescale of the order of one minute.
- **Coarsening:** diffusion of gas between bubbles causes some to grow and others to shrink, leading to an increase in mean bubble size. The timescale is about 10 minutes, but may vary.
- **Film rupture:** foam films that are too thin and weak will rupture, and eventually the whole foam will collapse and disappear. The timescale for these processes is hugely variable.

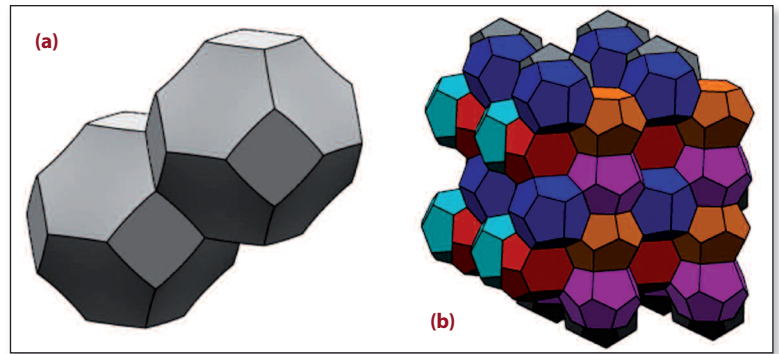
In what follows we shall be interested in timescales of a few minutes, for which the foam has had time to drain dry but gas diffusion is negligible, as is experimentally borne out by the fact that bubble sizes do not change appreciably. Under such circumstances, a dry foam can be seen as a structure that realises a partition of space into cells of given volumes for a minimal expense of surface area. When the cells all have the same volume, this is known as the *Kelvin problem* – by analogy with the Kepler problem of how to pack spheres so that they take up the least amount of space [5]. Kelvin was interested in using foam as a model for the luminiferous

▼ FIG. 1: A moderately wet 2D foam cluster. (Image by M. Fátima Vaz, Instituto Superior Técnico, Lisbon.)



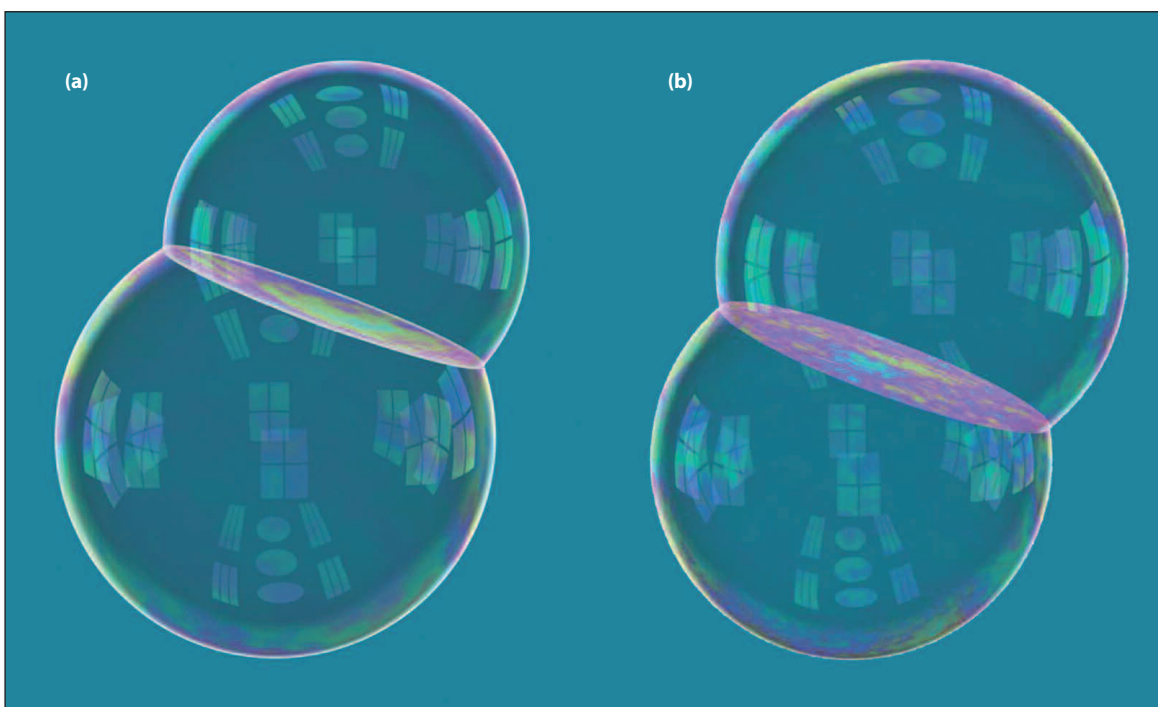
■ aether of electromagnetic theory, which was motivated by the need to find a material that would have zero compression modulus and therefore not support any longitudinal waves, as it was by then already known from experiment that electromagnetic waves were strictly transverse. The structure Kelvin came up with – a packing of identical 14-sided truncated octahedra, or, as he called them, orthic tetrakaidecahedra [6] (see figure 2a) – turned out to be a very good candidate for the division of space into equal volumes with minimal partitional area, until it was dethroned by the Weaire-Phelan, or A15, structure in 1994 [7] (see figure 2b). Unlike Kelvin's, this fills space with cells of two different shapes (but equal volumes), a dodecahedron and a 14-sided polyhedron. It beats Kelvin's by a slim 0.3%. However, there is no formal proof to date that the Weaire-Phelan structure, which was found by numerical minimisation of the energy of competing structures, is the lowest-energy geometry of a 3D foam. Indeed, formal proofs are very hard to come by in this field. Consider a related problem, known as the *double bubble conjecture*: given two volumes, V_1 and V_2 , what is the surface that circumscribes these two volumes with the least surface area? Not until 2002 was this proved to be two bubbles joined at a single film [8] (see figure 3); if $V_1 = V_2$, the film is flat.

The 2D version of the Kelvin problem concerns the minimum partition of the plane into regions of equal area. That it is the tiling by regular hexagons (or honeycomb) seems obvious, and yet stood as a conjecture since classical antiquity [9]; its formal proof has been given only recently by Hales [10].



▲ FIG. 2: (a) The Kelvin structure. (b) The Weaire-Phelan structure. (Images by Kenneth Brakke, Susquehanna University.)

In this article we discuss some of our own recent results relating to surface minimisation in 2D foams. The general strategy is to draw competing structures and compare their energies; these can be worked out analytically in some cases, more generally numerically by solving a small set of non-linear algebraic equations that implement Plateau's laws. In the spirit of Kelvin, we offer no formal proofs. Besides contributing towards the solution of an intriguing (and, in our view, aesthetically pleasing) riddle of discrete geometry, what do we expect to achieve by this? Many solid foams, traditionally viewed as a distinct subject, are actually formed by freezing of vitrifying liquid foams. The mechanical properties of solid foams, such as their Young and shear moduli, and their yield strength, are paramount in many of their structural applications, and are known to depend sensitively on their topology [1]. Knowing the topology and geometry of the precursor, liquid foam composed of cells of given sizes and number of sides would therefore allow a more accurate prediction, and thus enable tailoring, of the properties of the final cellular solid. Other possible applications will be discussed below.



◀ FIG. 3: The double bubble. (a) Unequal volumes. (b) Equal volumes. (Images by J. Sullivan, TU Berlin.)

How to pave a plane with two types of tile?

A straightforward generalisation of the Kelvin problem in 2D is to ask ourselves: What is the minimum-perimeter partition of the plane into regions ('cells' or 'bubbles') of *two* different areas? Without loss of generality we take the area of the cell with fewer sides to be unity; the other cell will then have (non-dimensional) area λ , the ratio of cell areas. Again we consider *perfectly dry foams*, *i.e.*, whose liquid content is close to zero: these obey Plateau's laws [3] in 2D, as above, with the only difference that films (which must be either straight lines or arcs of circle) meet at 120° angles at vertices. Plateau's laws are *necessary* conditions for perimeter minimisation, but do not uniquely determine the (stress-free) geometry of a tiling of given topology and given cell area ratio λ . In this first approach we restricted ourselves to periodic tilings with at most two cells of each area per repeating unit, and such that all cells of the same area are equivalent (*i.e.*, have the same neighbourhood). Under these restrictions there is a finite (and fairly small) number of possible arrangements. Figure 4 shows the five that are minimal, *i.e.*, that have the lowest energy in some range of λ . Their characteristics are summarised in table 1. We use a simple notation to label them, *e.g.*, 3_19_1 is a tiling with one 3-sided cell and one 9-sided cell per repeating unit, etc. In addition to these, there are four others that are never minimal: 2_110_1 , 2_210_2 , 3_29_2 and 6_26_2 .

Interval of λ	Minimal tiling
0.645-1	6_16_1
0.268-0.645	5_27_2
0.108-0.268	4_18_1
0.041-0.108	4_28_2
0-0.041	3_19_1

◀ **TABLE 1:** Minimal (*i.e.*, lowest-energy) tilings vs λ [12]. (With kind permission of The European Physical Journal (EPJ).)

It is seen that when cell sizes are very different (*i.e.*, for small λ), their numbers of sides are also very different. As λ increases the two types of cells become more similar; for $\lambda > 0.645$ they are both hexagons, and we go continuously to the monodisperse honeycomb limit as $\lambda \rightarrow 1$.

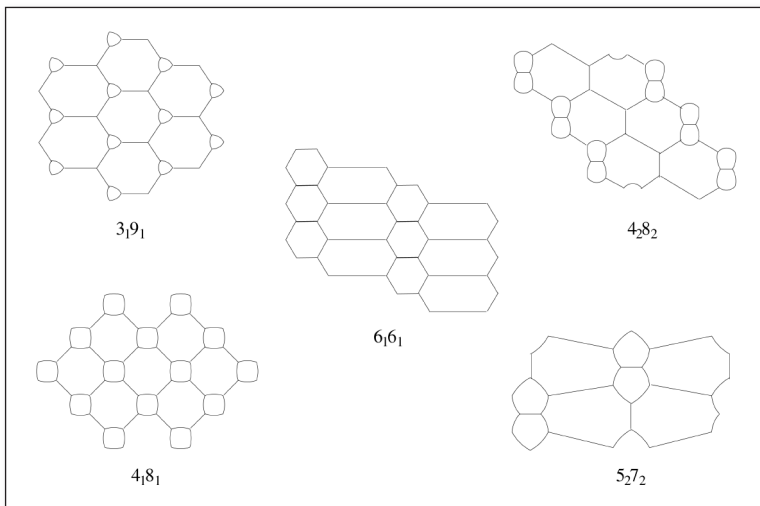
Mixing vs sorting

What happens if we now allow the cells to de-mix, *i.e.*, separate into two regions each composed of cells of just one size? And what if we are dealing not with an infinite foam, but with a (more realistic) finite cell cluster? We now need to consider, in addition to the five minimal tilings of figure 4, the four sorted arrangements of figure 5. Sorting is of course always into two honeycombs, since each contains only cells all of the same size.

Besides the 'bulk' energy of each tiling, we must estimate the energies of the outer boundaries of the clusters, and of the boundary between clusters of different-sized cells; the latter we approximate by that of a wall of dislocations between mismatched honeycombs. This we do for each cell area ratio λ and for each number N of bubbles of each size. Our results are summarised in figure 6: note the alternation between mixed and sorted states, where the winning sorted arrangement is always IV in figure 5 ('partial wetting' of one honeycomb by the other).

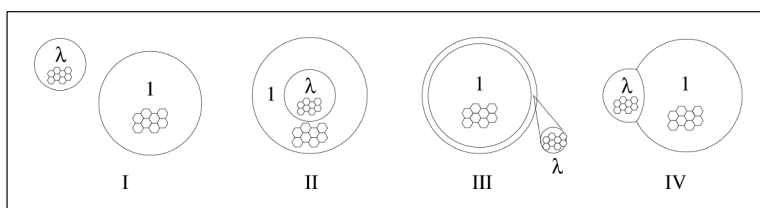
Smaller clusters want to be mixed because of the high relative cost of forming interfaces; as N increases, 'biphasic' regions appear. However, convergence to the $N \rightarrow \infty$ limit [11] is slow, and has not quite been reached for $N = 104$. Two further remarks are in order. Firstly, the limit of a monodisperse honeycomb is again approached continuously as $\lambda \rightarrow 1$, as expected (since in this limit $6+6$ and 6_16_1 become indistinguishable). Secondly, and more intriguingly, the size of the 'biphasic' regions increases with increasing λ , *i.e.*, as the two types of cells become *more similar*. This behaviour is opposite to what one normally expects in a binary mixture, where miscibility is usually favoured by particle likeness.

But why should we care whether cells/bubbles mix or segregate? More recent applications arise in the emerging field of *discrete microfluidics* [13]. Here one aims to



▲ **FIG. 4:** The five tilings that have minimum perimeter in some range of λ , the cell area ratio [11]. (With kind permission of The European Physical Journal (EPJ).)

▼ **FIG. 5:** The four sorted arrangements of honeycombs (I, II, III, IV) of cell sizes 1 and λ [11]. (With kind permission of The European Physical Journal (EPJ).)



control the transport and mixing (or sorting) of individual droplets of liquids for, *e.g.*, the delivery of minute quantities of reacting chemicals, as in tests of many different formulations of a novel drug or consumer product. Ideally one would like to be able to feed different reactants through the same channel(s) in such a way that they would not react until reaching some specified locations at specified times. Recent work [14] suggests that this might be achievable by encapsulating the chemicals in the bubbles of ordered foam structures that are then pushed through appropriately designed channel geometries. At low flow rates where viscous dissipation is negligible, whether bubbles mix or sort is governed by surface tension minimisation. In view of our results, careful selection of bubble sizes could therefore lead to the bubbles (and chemicals) self-assembling into the desired configurations, with no need for outside intervention.

Outlook

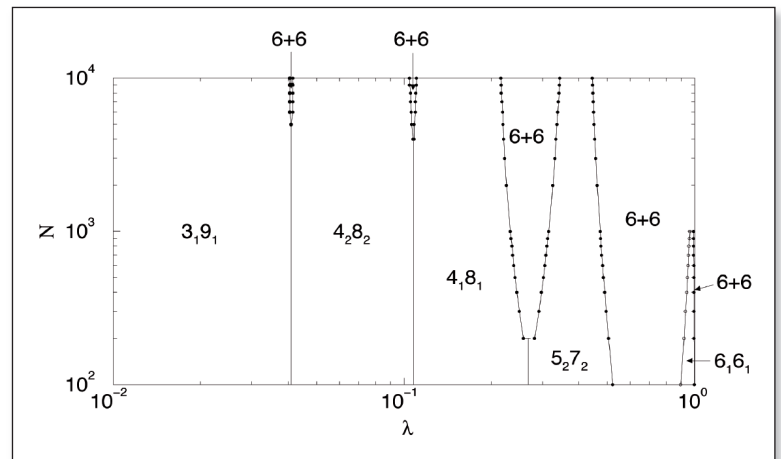
The work presented here can be extended in a number of directions. Our analysis of bidisperse tilings of the plane is admittedly rather restrictive. Ideally one would like to include a much larger set of possible arrangements, both periodic and aperiodic.

When addressing the competition between mixing and sorting Erreur ! Source du renvoi introuvable. we investigated just the special case of equal numbers of bubbles of each area. Moreover, we restricted our set of allowed mixed arrangements to those discussed above. The more general problem of finding the minimal configuration of clusters of bubbles of areas 1 and λ in any proportion would lead to the full phase diagram of 'bubble alloys'. One such diagram has been obtained by Likos and Henley [15] for a binary mixture of hard discs (in the $N \rightarrow \infty$ limit), using a 'zero-temperature approach' which, like ours, neglects the entropy. Their results for 1:1 clusters are in rough agreement with ours, the main differences being that they find an interval where a 'random tiling' wins, *two* intervals where 5_27_2 wins, and they did not consider the 4_28_2 tiling.

We have left out entirely the many issues pertaining to foams out of equilibrium, namely their rheology. These are currently the focus of much research, particularly with respect to the rigidity loss and flow of wet foams in relation to their topology. This and the applications to microfluidics alluded to above will probably be the most active fields of foam research in the coming years. ■

Dedication

This article is dedicated to the memory of M. A. Fortes, originator and prime mover of the research.



About the authors

Paulo Teixeira is a theoretical soft matter physicist. He gained a PhD from the University of Southampton (UK) and held postdoctoral positions in Amsterdam, Cambridge, Leeds and Lisbon. He is one of the first batch of *Outstanding Referees* of the American Physical Society. **Jorge Buescu** is a mathematician working on dynamical systems. He holds a BSc in Physics from Lisbon University and a PhD in Mathematics from the University of Warwick (UK). He has held teaching positions at the Technical University of Lisbon and at Lisbon University, and has authored several books on mathematics for the general public.

▲ **FIG. 6:** 'Phase diagram' of 1:1 cell clusters in the (N, λ) plane. (Adapted from [11]. With kind permission of The European Physical Journal (EPJ).)

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