An experimental realisation of the Weaire-Phelan structure in monodisperse liquid foam

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The Weaire-Phelan (WP) structure is the lowest energy structure known of an ideal monodisperse foam in the dry limit. Up to now it has not been realised in the laboratory. Instead Lord Kelvin's 1887 structure, which it supplanted in 1994, has repeatedly been found in attempts to produce an ordered structure. This paradox is attributable to the flat walls of the containers used, with which the Kelvin structure is more compatible. Accordingly, we have fabricated a patterned mould whose faceted walls conform to the WP geometry, and thereby succeeded in inducing the formation of perfect crystals of the WP structure. Foam samples consisted of approximately 1,500 bubbles. Vibrations favoured crystallization.

Keywords: foam; Kelvin problem; Weaire-Phelan structure; templating

1. Introduction

A liquid foam of very low liquid fraction is described as dry, and consists of films forming the curved faces of packed polyhedral bubbles. Kelvin's original conjecture [1,2] regarding the ideal structure of a monodisperse dry foam was a brilliant insight, worked out in fine detail. His personal quest for the division of space with minimum partitional area [1], which is the mathematical expression of the Kelvin problem, was not stimulated by any observation of real foams, but rather by abstract speculation on the structure of the ether of space.

The Kelvin structure is a crystal in which the bubbles are arranged on a body-centered cubic lattice, and take the form of a tiling by truncated octahedra (space group $Im\bar{3}m$). Although scepticism reigned in the context of his ether theory, Kelvin's structure attracted widespread interest thereafter, being seen as relevant to biology as well as physics and mathematics. Observations of truncated octahedral bubbles proved elusive in nature. In the laboratory, monodisperse dry foams grown in various kinds of containers, but all with flat or smooth surfaces, were found to have highly disordered structures, consisting of many cell types [3]. Similar distributions have been found in

numerical studies using periodic boundaries [4] and for a family of periodic structures with lower surface area than the structure proposed by Kelvin [5].

The Weaire-Phelan (WP) structure consists of two kinds of polyhedral bubbles, with twelve and fourteen sides respectively (space group $Pm\bar{3}n$). The structure can be cut along {100} planes, showing the existence of layers of bubbles (Fig. 1). Since its introduction in 1994 [7], it has played an important role in theory and simulation of foams, for example in the study of elastic properties [8]. The lack of an experimental counterpart to this theoretical construction continued the frustrating story of the Kelvin problem. Only one isolated instance of observation of a piece of the structure occurred in a microscopic examination of monodisperse foam [9], and it was never reproduced.

Ironically, after the announcement of the WP structure, large crystalline samples of the Kelvin structure were at last prepared by the group of Fortes[10] by confining equal size bubbles (diameter approximately 3 mm) between a liquid interface and a glass plate. An alternative production method employs columns of monodisperse bubbles less than about 0.4 mm in diameter, which order spontaneously into fcc or hcp crystals [11,12]. A transition to the Kelvin structure is achieved by either lowering the liquid fraction of the foam with an applied osmotic pressure [13] or by using column heights of a few centimetres [14].

One might ask why the WP structure never showed up in previous experiments. The answer seems to lie in the form of the containers used, which all had flat walls. This includes solid containers, but also the surface of the liquid/foam interface, which is always a plane under gravity in static conditions. The {110} faces of the Kelvin structure are well adapted to fit against such a surface, forming a surface pattern close to that of the honeycomb [15,16]. The WP crystal cannot be cleaved so as to present such a flat surface.

2. Experimental Method and Results

The challenge has remained: how can we create a crystal of the WP structure? To do so, we used the Surface Evolver software [17] to design a container, the walls of which were templated with the geometry of the WP structure (Fig. 2).

The structure was oriented in the most obvious way, with its {100} planes facing the template walls. This arrangement exhibits lines of prominent bubbles on a square lattice (or corresponding hollows if they are removed). The template was fabricated on an Object Eden 250™ 3D Printing System using Objet FullCure720™ translucent polymer with tolerance below 85μm. This allowed the construction of a pattern with the resolution required for the formation of the faceted surfaces.

In estimating the size of the bubbles which match this design, we roughly take account of the small proportion of liquid in the foam (which is in reality a function of vertical position and time). Supposing a liquid volume fraction of 0.1, the diameter of the required isolated bubbles is estimated to be 2.4 mm.

Once produced, the container is placed in a 1% by volume solution of the commercially available detergent Fairy Liquid in water. The container is inverted to remove any trapped air within the sample cavity. Equal sized bubbles are produced by releasing pressurised nitrogen gas from a glass capillary, of internal diameter roughly

0.3 mm, fixed in the surfactant solution at a constant depth. By varying the flow rate of the pressurised gas, the diameter of the bubbles may be chosen to match the scale of the template. Experiments were repeated with capillaries of different sizes in the range of 0.3-0.4 mm. Once the bubble size estimated above is found, determined by measuring the inter-bubble distances in a closed-packed 2D array of bubbles, the container is moved over the capillary to capture the bubbles being produced at a constant rate (4 to 45 bubbles per second, depending on capillary used). Sample filling is timed to control the number of bubbles captured. Once filled so that almost 6 full layers of bubbles have formed, the container is sealed by sliding a glass plate over the opening of the container. The closed container is then removed from the surfactant solution and the sample is manually shaken for a few seconds. It is then lit from above using a planar backlight while images are captured from below the sample using a Canon EOS 50D camera. From the photographs taken, it is immediately evident that the WP structure is formed. The samples, which are readily produced, contain perfect monocrystals of the structure without defects.

The ordered foam shown in Fig. 3, viewed along the <100> direction as in Fig.1b, comprises a total of about 1,500 bubbles stacked on six layers. The curved surface of the bubbles in the layer in contact with the solution optically deforms the inner details of the structure, allowing most of the edges to be clearly visible throughout the whole sample. In future work we will carry out experiments on larger samples (more than 10,000 bubbles) and use X-ray tomography to confirm the internal structure [14].

Bubble size is thought to be critical. The stated choice is of the same order as the capillary length $l_0 = (\gamma/ \rho\, g)^{1/2}$ (with surface tension γ, density of the solution ρ, gravitational acceleration g), so that, apart from the lowest bubble layer, the foam is fairly dry when in equilibrium under gravity. The extent of the wet layer is l_0^2/d, where d is the average bubble diameter [16]. The use of much smaller bubbles may be prohibited, because the WP structure is not stable for liquid fractions beyond about 0.15 [18].

3. Outlook

Continuing research will be devoted to other possible ordered foam structures, including the family of clathrates and structures such as those derived from the Frank-Kasper phases, which have been conceived and discussed for many years, but never realized [5, 19-21]. Achieving this will open the field to the experimental investigation of their properties. In addition, such samples could be solidified using gelling agents [22], opening up further possibilities to experimentation and application.

Finally, let us recall that foam physics was envisaged by W. L. Bragg [23], C. S. Smith [24] and others as a model system for crystallography and materials science at the atomic scale. The methodology that we have introduced here should offer opportunities to find new analogies and insights by studying the epitaxial growth of ordered structures and defect formation mechanisms on the scale of millimeters.

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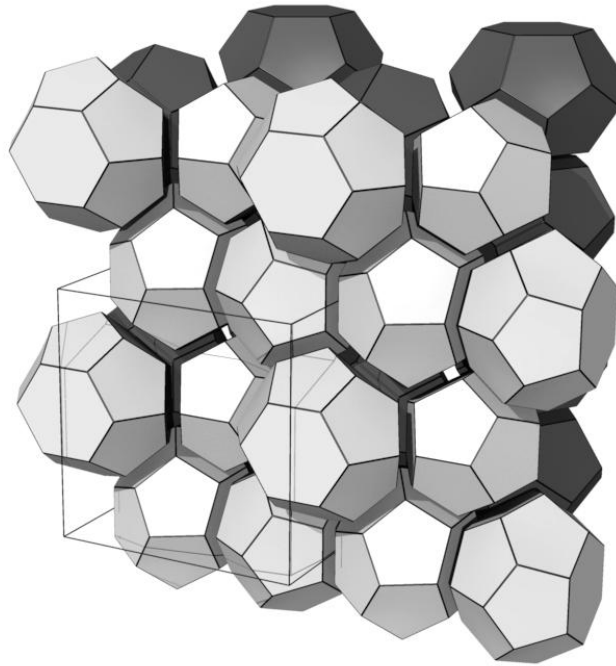
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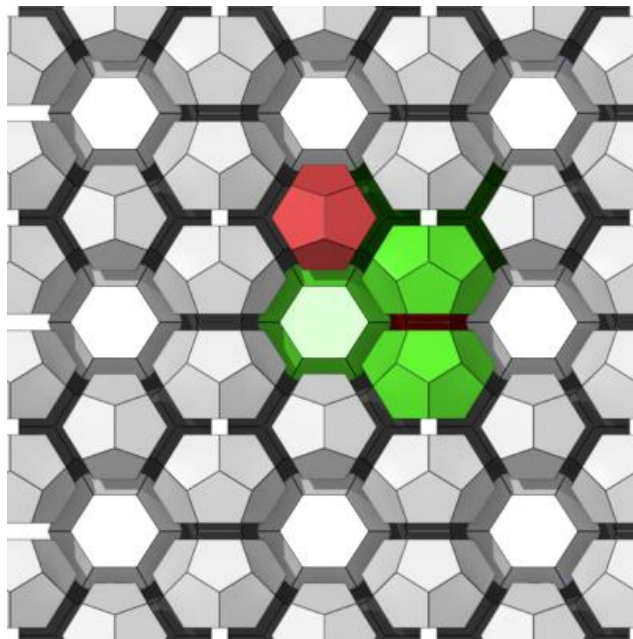
(B)

Figure 1. Computer generated exploded views of two layers of bubbles in the WP structure. (A) Bubbles centers in each layer lie on two parallel {100} planes. (B) Frontal view, with the A_3B periodic unit shown in color. (Images generated with 3dt [6]).

Figure 2. Photograph of the template used to produce the Weaire-Phelan structure. The template is placed in a surfactant solution, to receive bubbles emitted from below. Inner surfaces correspond to {100} faceted planes of the WP structure (sample dimension 41x41x20mm; lattice spacing 4mm; volume available to each bubble 8mm^3; maximum number of bubbles 16x16x7=1792).
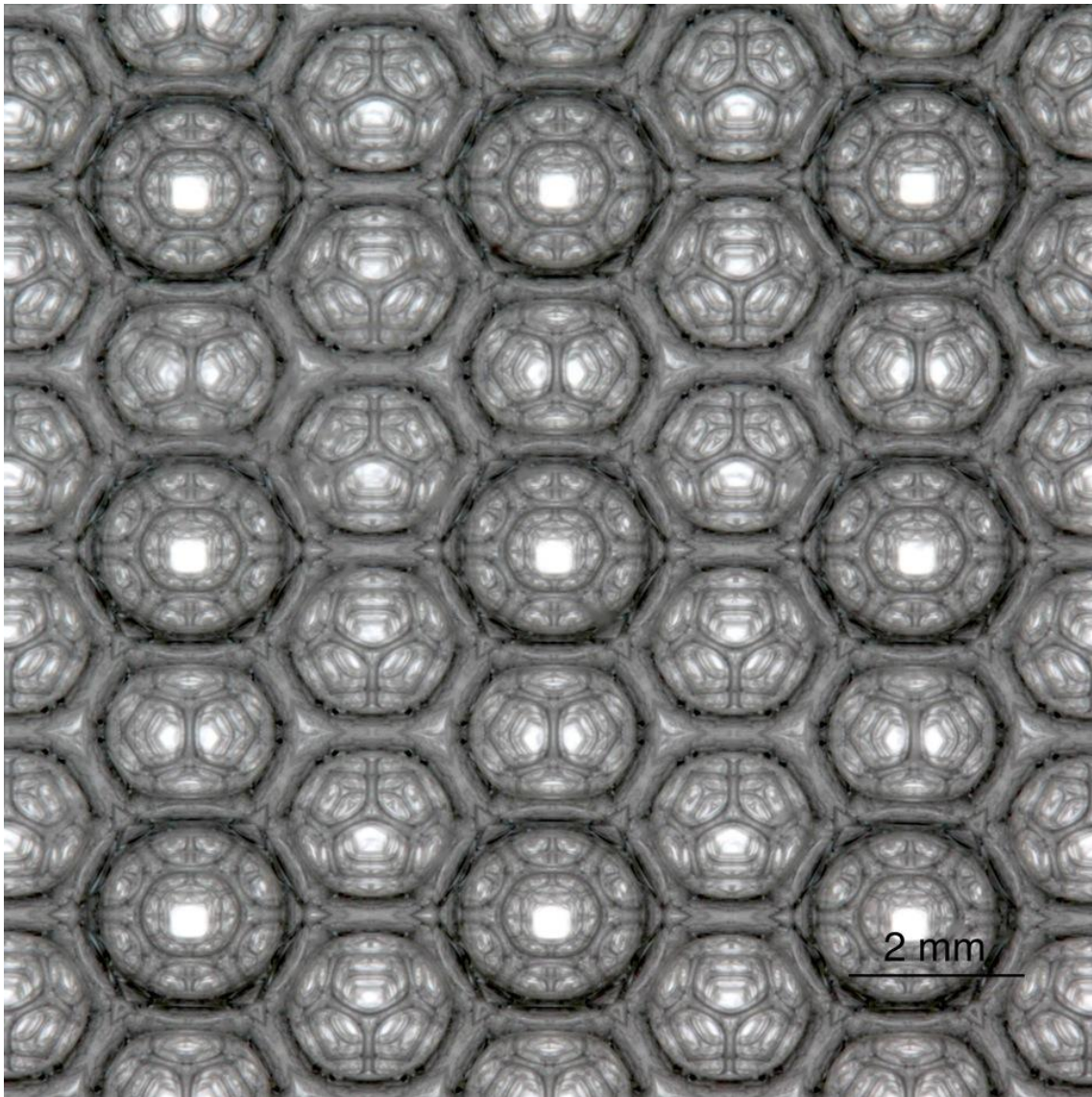
Figure 3. Photograph of the experimentally produced Weaire-Phelan foam viewed along its <100> 2-fold axis of symmetry. The sample contains approximately 1,500 bubbles, arranged into 6 layers. Many fine details are observed confirming the absence of defects.