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LETTER TO THE EDITOR

Vertex instabilities in foams and emulsions

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Abstract. Plateau's rules, which are the basis of most descriptions of foam structure, include one which dictates that junctions of more than four Plateau borders are always unstable. This has been rigorously proved by Taylor for the idealized mathematical model in which the borders are reduced to lines of infinitesimal thickness. Nevertheless we here present a mathematical analysis which shows that a symmetric eightfold vertex is metastable, even for arbitrarily thin Plateau borders. This paradoxical result, contrary to conventional wisdom, was first suggested by computer simulations and some simple experiments.

In the middle of the 19th century, J A F Plateau investigated the rules of equilibrium of conjoined soap films and analogous interfaces, eventually gathering together his findings in a classic book (Plateau 1873). The rules were essentially empirical. A full mathematical justification of them was to appear a century later (Taylor 1976, Almgren and Taylor 1976).

One of the rules states that a vertex formed by more than four soap film edges coming together at a point is necessarily unstable. A celebrated example of such a vertex is shown in figure 1(a). Plateau observed it to be unstable, distorting spontaneously to form the structure of figure 1(b). An extra quadrilateral face appears, and the eightfold vertex dissociates into four fourfold ones.

The vertex instability rule refers to so-called dry foam, in which the liquid content is so low that one readily adopts the mathematical idealisation of soap films as surfaces with no finite thickness. These meet on lines, which in turn meet at the vertices in question. In reality, the lines which meet at the junctions are thickened to form finite Plateau borders, as in figure 2. The action of gravity on a typical soap froth reduces the liquid fraction to a very low value in equilibrium. In such a froth, the rule is commonly seen to be obeyed, in that all vertices are observed to be fourfold. The conventional wisdom has therefore been that the rule applies at, and close to, the dry foam limit (Weaire 1994). Our purpose here is to show that this is not strictly correct.

We do not call into question the proof of instability for the idealized dry foam itself. Rather it is claimed that the symmetric eightfold vertex is stable (or rather metastable) for any finite liquid fraction. This metastability becomes more and more precarious as the dry limit is approached; the range of distortion for which the system is stable decreases to zero. There is no contradiction to the established theorem.

The first clue that something was lacking in our conventional description of vertices and their stability was found in simulations of ordered foam by ourselves and others (Phelan *et al* 1995, Kraynik 1995), using the Evolver program (Brakke 1992). In these simulations a wet foam whose cells are arranged in the face-centred cubic structure remains stable down to the lowest values of liquid fraction which can be reliably treated at present. These are

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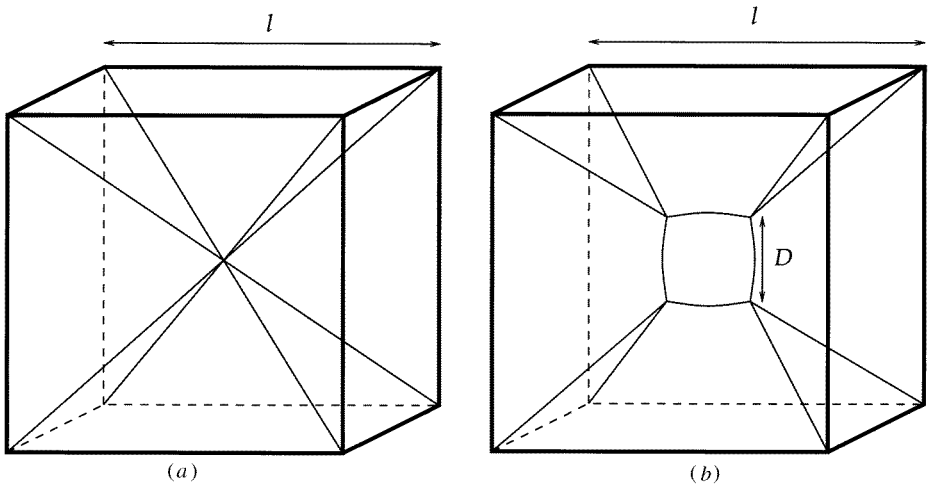

Figure 1. (*a*) Twelve films meeting along eight edges at a single vertex inside a cubic frame. (*b*) The eightfold vertex shown in (*a*) above has split into four tetrahedral vertices. This is the configuration of films inside a cubic frame reported by Plateau.

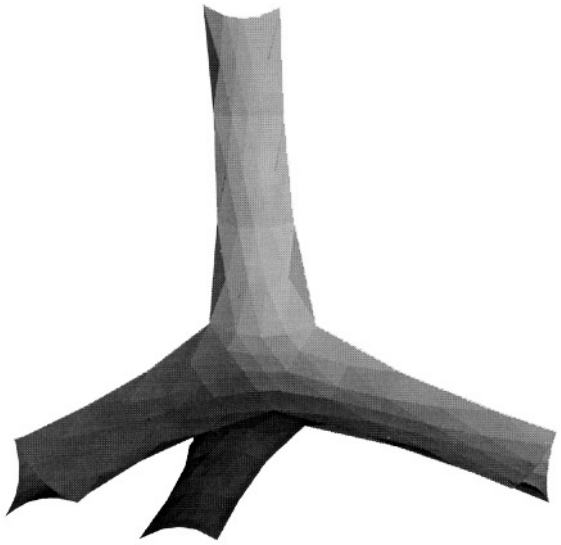

Figure 2. Detail of a single tetrahedral junction and its four borders.

of the order of 1%. The structure exhibits the kind of vertex whose skeleton is shown in figure 1(a). No instability of the kind anticipated on the basis of Plateau's rules was found.

At first we were inclined to attribute this to some failure of the algorithm, or some restriction due to the boundary conditions. We were eventually driven to fully reconsider both experiment and theory. Both reinforce the conclusion that provided that the cubic symmetry of the boundary conditions is preserved, *the multiple vertex depicted in figure 1(a) is metastable for any finite liquid fraction.*

Plateau's original papers on this matter make very interesting reading (Plateau 1873). He performed a number of variations on his basic experiment, which is simply to withdraw a

wire frame from a soap solution, and observe the structure which is formed. In the case of a cubic frame one observes the configuration shown in figure 1(b). Plateau sometimes used a combination of two liquids, which would correspond to an emulsion, rather than a foam. In this way he could form systems in which the two phases occupied comparable volumes, and he observed the multiple vertex under some conditions. But his clear conclusion remained that only the fourfold vertex was stable close to the limit in which the Plateau borders are thin (the dry foam limit), since he did not observe higher vertices in equilibrium in such a case.

In recent work on foam drainage (Weaire *et al* 1993) we have introduced a technique for creating wet foam structures in quasi-equilibrium, simply by feeding the foam with a continuous supply of liquid from the top. At least for low flow rates (and hence low liquid fraction) the foam seems to remain close to the static equilibrium structure. We were thus led to do the same thing with Plateau's wire frame experiment, in order to gain insight into vertex stability.

The details of this simple experiment will be described elsewhere (Weaire *et al* 1995). Here it is sufficient to note that an eightfold vertex which is created by increasing the flow rate persists when the flow rate is decreased to very low levels. These are such that the Plateau border width is reduced to less than a millimetre, while the wire frame has dimensions of the order of centimetres. The evident metastability of the eightfold vertex, in contradiction of theoretical expectations, gave further motivation for the following semi-quantitative analysis.

We wish to understand the dependence of energy, which is just the surface area in this problem, upon structure and liquid content. We make an expansion of the kind suggested by Weaire (1994), in which successive corrections are added, starting from the dry limit. These incorporate firstly the contribution of the Plateau borders, and then the junctions (vertices), both of which increase as the amount of liquid is increased. This kind of expansion, developed here for one special case, should prove generally useful for a variety of purposes.

Firstly we examine the dry foam, and estimate the energy, which is simply the total film area, as a function of the edge length D of the additional square face introduced by the supposed instability. By considering the work done by surface tension forces, it is easily seen that the energy varies quadratically with D. We estimate this variation using a planar approximation for the films, with the result shown in figure 3.

Some idea of its reliability is provided by the estimate of the equilibrium size of the square face. For a cube of side length l we find a minimum with respect to D at $D = 0.073l$. Experiment suggests $D \approx 0.16l$. The difference is attributable to the approximation of planar faces. Most of the succeeding argument is less less susceptible to this kind of error, and it is in any case intended to be semi-quantitative.

The quadratic term in D is negative as expected, and of magnitude

$$\left.\frac{\partial^2 E}{\partial D^2}\right|_{D=0} = -0.12 \tag{1}$$

independent of l. This corresponds to the instability which we have described. Note that we have chosen the surface energy to be 2σ, where $\sigma = 1$ since each thin film corresponds physically to *two* gas–liquid interfaces (or liquid–liquid in the case of an emulsion). Plateau border surfaces are single interfaces.

We now consider the effect of a finite liquid fraction (ϕ_l). Geometrical arguments (described below) lead to an expansion of the form

$$E = E_d + E_l \phi_l^{1/2} + E_v \phi_l + \cdots \tag{2}$$

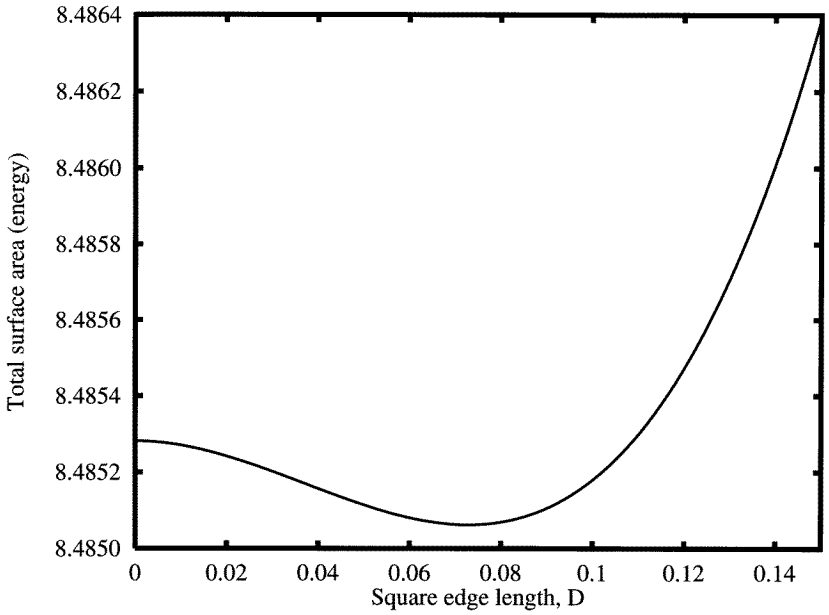

Figure 3. Total surface area (energy) as a function of the square edge length D for a planar approximation to the configuration of figure 1(b). The frame side length l is set to 1.0.

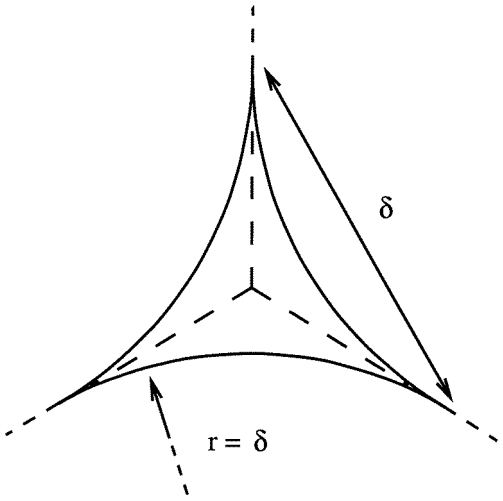

Figure 4. Cross section of the idealized Plateau border used to estimate the edge correction. We define the border width, δ, as shown.

where the first term is the energy of the dry system, the second is the correction due to widening of the lines (figure 4) and the third makes a final correction for the thickening of the vertex. We shall call these the line and vertex corrections. We will truncate the expansion at this point.

The line correction, $E_l\phi_l^{1/2}$, is easily estimated. If ϕ_l is small we can idealise the Plateau borders as having the regular cross section shown in figure 4, i.e. three tangential circular

arcs of equal radii. We define the width of the border, δ, as shown. Note the equality of δ and the arc radius (equivalently the Plateau border curvature or *pressure*). Ignoring the liquid volume localized at the vertices, there is an obvious relationship between ϕ_l and δ. If V_l is the liquid volume and V the total volume of gas and liquid then by definition $\phi_l = V_l/V$. But

$$V_l = LA_{pb}(\delta) \tag{3}$$

where L is the total line length and the Plateau border cross section, A_{pb}, is easily shown to be approximately $0.16\delta^2$. Equation (2) can be thus be recast in terms of δ and δ^2 (exact in the limit $\delta \to 0$).

The energy reduction per unit line length due to the formation of the Plateau border, as in figure 4, is

$$\Delta E_l = -0.32\delta. \tag{4}$$

To obtain the corresponding contribution to the energy we must multiply by the total line length. We therefore need to calculate the variation with D of the line length, L, inside the cubic frame. For simplicity we shall consider only the leading term, linear in D, which is:

$$\left.\frac{\partial L}{\partial D}\right|_{D=0} = -0.62 \tag{5}$$

Combining (4) and (5) we obtain a positive energy correction, linear in D and δ, i.e. one which favours stability. Indeed this is an important term in the argument, which cannot be pursued in terms of vertex energies alone. Balancing this correction against the quadratic term (1) yields a provisional estimate for the limiting point of stability before considering the effect of the third term in (2), that is, the vertex correction. This estimate is $D \approx 0.8\delta$ corresponding to a local maximum in E (see figure 5), and an energy barrier E_s of magnitude

$$E_s = 0.12\delta^2. \tag{6}$$

It is not to be inferred that the total energy varies linearly with D at $D = 0$, where a quadratic variation is to be expected. For D less than some value, of order δ, which corresponds to the separation of the eightfold vertex into four fourfold ones, there is a substantial correction from the vertex term. We do not attempt here to calculate the detailed variation of energy with D below this value: it suffices for our purposes to estimate the vertex correction, ΔE, for one symmetric eightfold vertex relative to four symmetric fourfold ones. The process of dissociation of the vertices is rather like a chemical reaction:

$$V_8 \Rightarrow 4V_4 + \Delta E. \tag{7}$$

We assume that E varies smoothly between the points indicated in the sketch shown in figure 5. Since the loss of stability and the separation of the vertices appears to occur at roughly the same value of D, a reasonable estimate of the stability criterion is

$$E_8 - 4E_4 < E_s \qquad \text{for stability.} \tag{8}$$

We have estimated the vertex corrections by fitting the Evolver results for the fcc and bcc structures to appropriate functional forms of the kind indicated above (equation (2)). The quadratic dependence of this term on δ can be inferred from a simple polyhedral vertex model. Full details will be given elsewhere (Weaire *et al* 1995). As an aside, it is interesting to note the quality of these fits. They provide a remarkably accurate relationship between energy and liquid fraction over a wide range and offer a reliable parametrization for many purposes, at least for these structures.

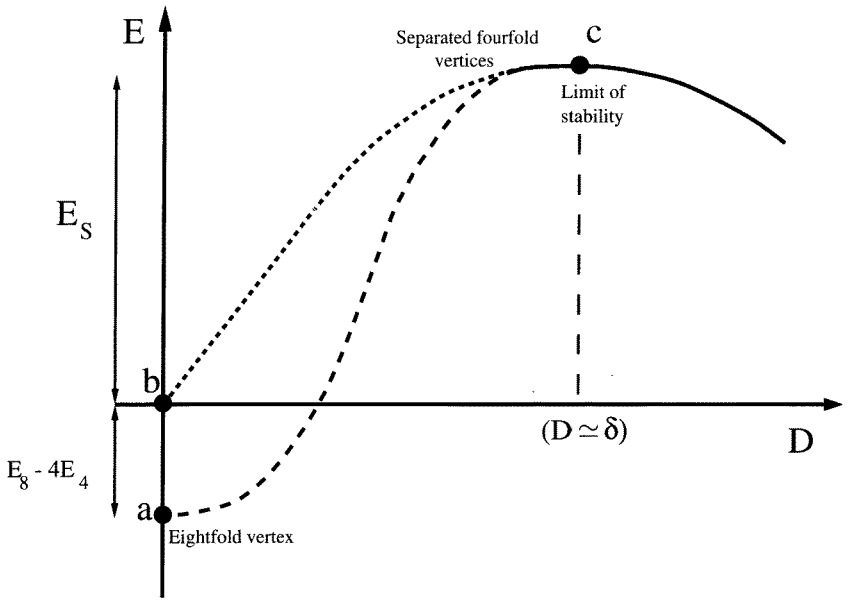

Figure 5. Schematic dependence of energy on D as an eightfold vertex dissociates to form the structure in figure 1(b). Neglecting vertex corrections this follows the curve bc. Including the vertex correction $E_8 - 4E4$, the expected variation is that of the curve ac.

In this way we obtain

$$\Delta E_8 = -0.34\delta^2$$
$$\Delta E_4 = -2.1\delta^2 \tag{9}$$

so that $E_8 - 4E_4 < 0$ and hence certainly less than E_s. The condition (7) is clearly satisfied. We conclude that the eightfold vertex is indeed stable.

It must be pointed out however that we are comparing fourfold and eightfold vertices at constant δ (Plateau border pressure) and not at constant ϕ_l. The approximations used have been limited to terms of order D^2, $D\delta$ and δ^2. The corrections needed to convert the result to one in terms of liquid fraction are of higher order but may be numerically significant.

With this reservation we have arrived at the surprising conclusion anticipated in our introduction. Higher vertices of this and presumably other kinds are actually stable for real systems. They are however metastable and hence are not readily formed for low liquid content. In the present case, the energy increases only up to the point indicated in figure 5, that is,

$$D \approx \delta. \tag{10}$$

This metastable range shrinks to zero as the liquid fraction, and hence δ, decreases. Note also that this metastability is dependent upon the symmetry of the vertex.

In further work we will analyse the effects of asymmetry both experimentally and theoretically. A related problem is the contribution of internal distortions to elastic moduli, particularly $\frac{1}{2}(c_{11} - c_{12})$ which corresponds to tetragonal distortion. The scaling of the various terms considered above is such that the second derivative of energy with respect to D should remain finite as $\delta \to 0$. This means that the elastic modulus should show no anomalous behaviour, even in that limit.

Typical foam structures are disordered. This, together with the narrow range of metastability, accounts for the absence of multiple vertices in such a system; Plateau's generalization was correct, in practical terms. However there is great current interest in ordered structures (Weaire and Phelan 1994a, b, Phelan *et al* 1995), such as fcc and bcc. The ideas presented here and particularly the expansion used will assist us in better understanding the role of multiple vertices in such cases, now that we have learned to accept them.

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Note added in proof. Brakke (private communication) has indicated that negative Hessian eigenvalues (indicative of instability) have been found in some calculations for higher-order vertices using the Evolver. However, since our conclusions rest on multiple grounds we will present them, pending a resolution of the doubt which this raises.

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