

Determinism and stochasticity in ideal two-dimensional soap froths

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ABSTRACT

It is shown that, owing to considerable stability of small cells with respect to neighbour switchings, the evolution of a two-dimensional soap froth during coarsening frequently passes through situations of fourfold and fivefold vertex decay. These situations require additional assumptions to be resolved.

§1. INTRODUCTION

The evolution of a two-dimensional (2D) soap froth has received some attention recently, and has been studied both theoretically and experimentally because of its puzzling regularities (Aboav 1980, Weaire and Kermode 1983, 1984, Weaire and Rivier 1984, Beenakker 1986, 1988, Mullins 1986, 1988, Wejchert, Weaire and Kermode 1986, Glazier, Gross and Stavans 1987, Marder 1987, Fradkov and Udler 1989, 1990, Glazier, Anderson, Grest and Stavans 1989, Stavans and Glazier 1989, Stavans 1990, Peshkin, Strandberg and Rivier 1991). This evolution not only is interesting *per se* but also is usually considered to provide valuable insight into other important phenomena, for example grain growth in polycrystals (see references above and also Smith (1952, 1964), Fradkov, Shvindlermann and Udler (1985) Anderson (1986) and Fradkov (1988)).

Experimentally, a quasi-2D froth is realized by squeezing soap froth between two well polished parallel glass plates (a Hele-Shaw cell), so that the distance between the plates is smaller than the characteristic size of the cells (Smith 1964, Glazier *et al.* 1987, Stavans and Glazier 1989). Excessive liquid can be automatically drained out through

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the network of walls (Plateau 1873). The gas can diffuse through walls and hence from one cell to another; the flux is proportional to the pressure difference between the cells. This diffusion process causes geometrical and topological evolution of the structure.

The froth is called ‘dry’ when the thickness of the walls is much smaller than the average size of the bubbles. In this case the relaxation time for reaching mechanical equilibrium (defined by the viscosity of the liquid) is much less than the time scale of the volume (area) changes due to gas diffusion. The latter can therefore be treated as an adiabatic process with respect to mechanical equilibration; this means that *from the viewpoint of the slow time scale* the froth is always in mechanical equilibrium. Thus the walls are circular arcs with curvature proportional to the pressure difference between the cells that they separate. For obvious topological reasons, no fewer than three walls can impinge on a vertex. Vertices of multiplicity higher than three are rarely, if ever, observed, because they are unstable and reduce immediately into threefold vertices. They are, however, of great importance because the topological evolution of the system passes necessarily through these situations.

Traditionally, an ideal 2D soap froth is considered as an assembly of cells divided by infinitely thin flexible walls. The walls are considered to be elastic lines which can extend, shrink and disappear *but not break* to decrease the total energy of the system, which is proportional to the total length of the walls. The cells contain incompressible gas; physically, the external atmospheric pressure is much greater than the pressure difference between the cells. Since all the walls have the same surface tension, mechanical equilibrium for triple vertices is achieved when the angles between adjacent tangents at the vertex are 120° . On the basis of this ideal model, Von Neumann (1952) derived the well known relation for the rate of change in the area of an individual cell with time:

$$\dot{A} = k(n - 6), \quad (1)$$

where \dot{A} is the area, n is the number of walls of the cell (the topological class) and k is a constant having the dimensions of diffusion coefficient. This relation implies that cells with $n > 6$ grow, those with $n = 6$ do not change their area, and those with $n < 6$ shrink in size until they eventually disappear. The decrease in the total number of cells due to these vanishings causes growth of the average area of cells, and hence coarsening of the ideal froth.

Equation (1) suggested an efficient way to study 2D soap froth evolution in terms of bubbles areas and topological classes, and corresponding distribution functions (Fradkov *et al.* 1985, Beenakker 1986, 1988, Marder 1987, Fradkov 1988, Fradkov and Udler 1989, 1990, Peshkin *et al.* 1991). The main difficulty in this study lies in the way that the topology of the system changes during evolution, that is how the so-called topological rearrangements occur. This is the issue which we address in this paper. In the next section we shall describe all possible topological rearrangements in the ideal system. We shall see that some of them (related to cell vanishings) could cause stochastic behaviour if they occur. Then we present a detailed investigation of the possibility of such vanishing events.

§ 2. TOPOLOGICAL REARRANGEMENTS

An important property of the ideal froth is the separation of time scales of the slow diffusion-controlled change in the areas, and rapid mechanical equilibration of shapes and lengths of the walls to maintain equilibrium vertices.

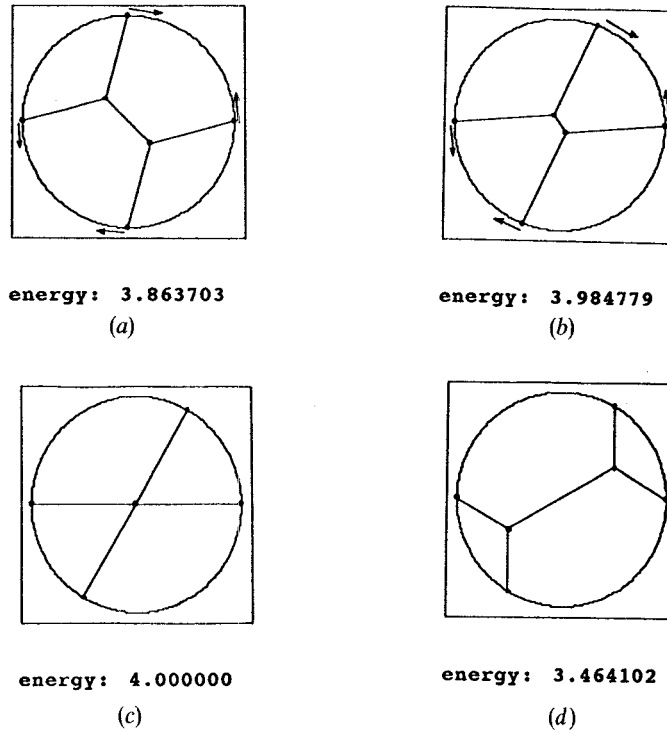
The two major implications are

- (1) the strictly non-local nature of evolution and mechanical equilibrium established at all times for the whole system, and
- (2) the smooth and continuous evolution of the structure, as small variations in areas due to the diffusion of gas cause small adjustments in pressures, shapes and lengths.

There are moments when this continuity is broken. At some point the length of a wall may become zero, so that two threefold vertices collide along this wall, forming an unstable fourfold vertex. It is always energetically favourable for this vertex to reduce into two new threefold vertices with a new wall of finite length between them. This topological transformation is called neighbour switching, because of the changes in the connectivity of the four participating cells (fig. 1). At the moment that this takes place, areas do not change, but the pressures, lengths and curvatures change in a discontinuous way. Given the geometry of the froth with a fourfold vertex it is always possible to determine the geometry after the switching. This means that switchings are deterministic events in the ideal froth.

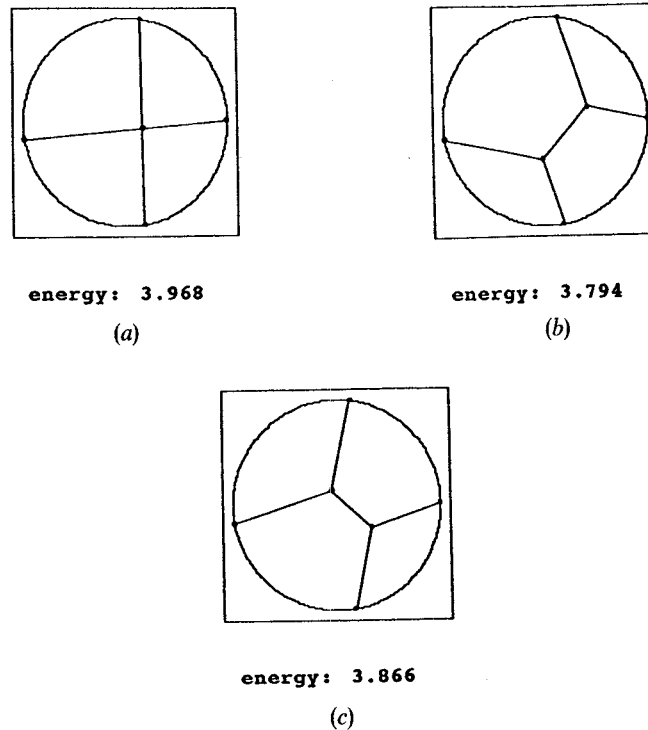
A different situation arises when a cell with number of sides $n < 6$ becomes very small and has to disappear. The only way for such a cell to vanish as a whole is to shrink to a vertex of corresponding multiplicity, which for multiplicities higher than three would immediately reduce into several threefold vertices. We do not consider here two-sided cells, which should not appear during the coarsening, as shown by Weaire and Kermode (1984).

Fig. 1



Different stages of neighbour switching with corresponding energies.

Fig. 2

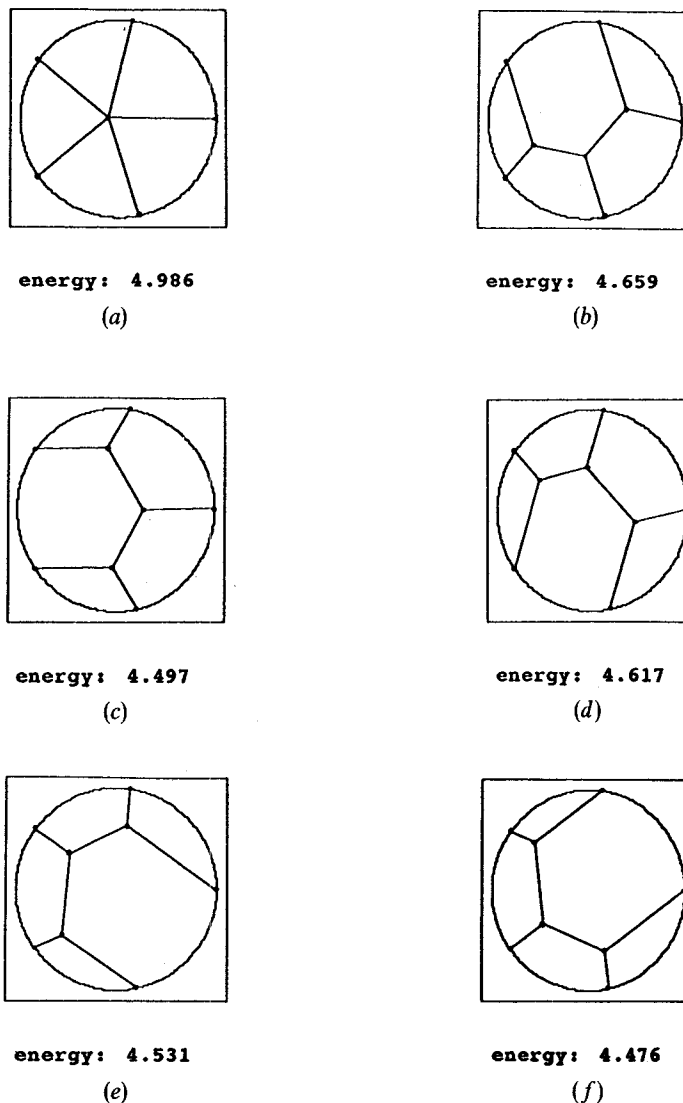


The two possible configurations after a fourfold vertex decay have energies less than the configuration with the fivefold vertex itself.

For a fourfold vertex there are exactly two ways to reduce; for a fivefold vertex there exist five different final configurations. Any infinitesimal decay of the multiple vertex is irreversible. It is important to realize that more than one final configuration can have an energy smaller than that of the multiple vertex. This is illustrated in figs. 2 and 3, which represent different final configurations after reduction of four- and fivefold vertices by energy minimization. The outer ends of the walls without loss of generality are fixed at some positions on the circle, and the walls are taken to be straight lines. In all these cases, all the final configurations have energies smaller than the initial energy. This means that reduction of a multiple vertex is an event which cannot be resolved within the framework of the ideal froth model; the model (as classically defined or implied) is incomplete since *it lacks a specification* of how to reduce multiple vertices to triple vertices.

The formal reason for the need of this extra specification is the following. Assume, as given, equations of motion having well separated fast and slow time scales, so that the slow time scale can be treated as an adiabatic perturbation. It is well known from the classical theory of differential equations that in this case, as long as there exists a stable equilibrium of the fast time scale, the slow time scale smoothly follows it. If eventually the stable equilibrium ceases to exist, the fast time scale will be awakened until a new stable equilibrium is found. The jump between stable equilibria is made on the fast time scale and hence depends strongly on how its dynamics is implemented, not only near

Fig. 3



The five possible configurations after a fivefold decay have energies less than the configuration with the fivefold vertex itself.

the equilibrium points, but also away from them. This is the situation in the ideal soap froth; the stable mechanical equilibrium of the wall network is lost when a higher-connectivity vertex is created, and therefore a new stable equilibrium position will have to be found. If several vertices are available, the vertex to be chosen will depend on the dynamics of the mechanical time scale away from equilibrium. However, in the ideal 2D froth model, these dynamics have never been stated; we only know that the stable equilibria correspond to minimization of the length of the network, but we do not know how this minimization proceeds away from a minimum. More specifically, since the jump occurs on the fast time scale, we have no right to assume that the walls of the

intermediate configurations are circular arcs, or to assume that the angles at the vertices are 120° or less; there are therefore too many ways in which a multiple vertex could decay. Only by specifying the total dynamics of the mechanical equilibration are we able to resolve the multiple vertex decays.

The important issue is therefore whether an ideal froth would, during its evolution, ever pass through configurations with multiple vertices. The traditional picture, dating back probably to the early paper of Smith (1952) and appearing quite plausible at first glance, is that, when a cell becomes very small, its walls become very short and is likely to undergo a switching. Therefore eventually it will vanish as a three-sided cell. Moreover, from this point of view the shortest side simply should switch first. Thus, in this picture, only ideally symmetrical four- or five-sided bubbles with equal lengths of all walls can disappear without losing sides and becoming three sided. Such situations obviously have a negligible probability, and therefore the ideal soap froth may be considered to be a complete model.

In the next section we consider this issue in detail; we shall show that the set of configurations in which a four- or five-sided bubble may disappear without losing sides is not negligible at all.

§ 3. ASYMPTOTIC BEHAVIOUR OF VANISHING CELLS

Let us assume that we have a vanishingly small four- or five-sided bubble. This implies that its walls possess relatively high curvatures and the pressure differences between the cell and its neighbours are much higher than the pressure differences between the neighbours themselves. In this limit the following statements are true.

- (a) All the walls of the small shrinking cell have the same curvature but may have different lengths.
- (b) All the walls that join the vertices of the cell from outside have negligibly small curvatures, compared with the curvature of the walls of the cell and may be considered as straight lines in its vicinity.
- (c) The characteristic time of life of the cell before the vanishing is small compared with the characteristic time for changes in the geometry of the neighbouring cells.

Under these conditions the shape of the vanishing cell appears to be very much restricted; uniform curvature of the walls combined with fixed angles of 120° or less in vertices imply that the lengths of the walls fully define it. These lengths in turn are defined by the angles between the corresponding outgoing walls:

$$L_i = R \left(\alpha_i - \frac{\pi}{3} \right), \quad (2)$$

where L_i is the length of the i th wall of the bubble, α_i is the angle between the outside (straight) walls connected to it and R is a uniform radius of curvature. Thus the shape of the cell is fully determined only by the angles between the outside straight walls and will not change, except for overall scale, until it completely vanishes, assuming that the angles are not changed externally. We can really consider them to be constants, because of the above-mentioned assumption (c) and the requirement of mechanical equilibrium of the cell as a whole. The latter means that the sum of external forces (the tensions of

the uniform outgoing walls) should be zero. This allows us to write the following relations for the angles α_i between outgoing walls:

$$\sum_{i=1}^n \alpha_i = 2\pi, \tag{3}$$

$$\sum_{i=1}^n \sin\left(\sum_{j=1}^i \alpha_j\right) = 0, \tag{4}$$

where n is 4 or 5. The final condition is

$$\sum_{i=1}^n \cos\left(\sum_{j=1}^i \alpha_j\right) = 0. \tag{5}$$

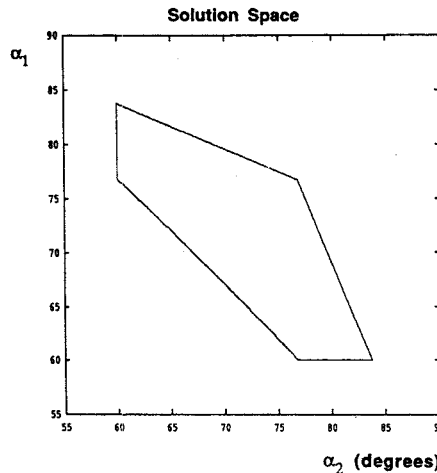
The solutions, if they exist, then have $n - 3$ degrees of freedom: only one degree of freedom for $n = 4$ (say α_1) and two for $n = 5$ (say α_1 and an adjacent angle α_2).

There is also a set of constraints, namely that the walls of the bubble cannot have negative lengths. These constraints imply that for the α_i we have

$$\alpha_i > \frac{\pi}{3}. \tag{6}$$

If conditions (6) do not hold, then the external geometry does not allow the existence of a small equilibrium cell, and hence the cell cannot disappear as a whole without losing one or two neighbours by switchings. Otherwise we can expect scaling behaviour of the vanishing cell. For $n = 4$, eqns. (2)–(4) imply that the opposite angles stay equal to each other and the cell has two axes of symmetry, as a rectangle with curved sides; eqns. (3) and (6) say that the allowed region of scaling behaviour is $\pi/3 \leq \alpha_1 \leq 2\pi/3$. The region of existence of scaling behaviour preserving the shape of five-sided cells is given in fig. 4.

Fig. 4



The region of existence of scaling behaviour preserving the shape for five-sided cells in coordinates α_1 and α_2 .

§4. CONCLUSIONS

We have shown that, contrary to conventional wisdom, the vanishings of cells in an ideal 2D froth may occur not only for $n=3$ but also quite probably with $n=4$ and $n=5$. Thus fourfold and fivefold vertices would appear. Their decay cannot be resolved within the framework of the classical model and further assumptions should be stated.

For example, one could take into account the finite distance D between plates and the finite width d of the walls in a real 2D soap froth. If $D \ll d$, we have some liquid filled region rather than a point after a grain vanishing. If the asymptotic shape of the grain is asymmetrical, so is this region and the way that it decays is predictable. Thus a fourfold vertex probably becomes, after it shrinks a short line (of finite thickness), directed along its longest axis, ready to nucleate two new threefold vertices.

On the other hand, when $d \ll D$ and the bubble is sufficiently small, three-dimensional effects will be noticeable, such as a capillary instability. As a result, the bubble may become conical, and a multiple vertex may exist in the bottom plate while a bubble still exists in the top plate of a Hele-Shaw cell. The details of this situation may depend on factors usually neglected, for example roughness of the plate surfaces, and may look, when two-dimensionality is regained after the decay, stochastic. More expanded discussion of the effects of finite thickness can be found in the paper by Stavans (1990) and in Bolton and Weaire (1990, 1991, 1992). An important open question is whether the difference between the two limits may or may not lead to dissimilar macroscopic behaviour in the long-time asymptotic regime.

It should be emphasized that the behaviour of vanishing cells is one of the central issues in the theory of froth coarsening because of the implications for the kinetic equation (Marder 1987, Fradkov 1988, Fradkov and Udler 1989).

The issue of stochasticity for 2D grain growth, which has just one time scale (determined by the mobility of grain boundaries) and where the width of the boundaries is about interatomic length, is considered in a sequel to this letter.

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