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# Wet two-dimensional bubble clusters: liquid partitioning and energy 

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#### Abstract

We address the problem of how liquid is partitioned among Plateau borders in wet two-dimensional foam clusters, and how vertex decoration by Plateau borders changes the bubble areas and the cluster surface energy. We show that the surface energy of wet free clusters of given liquid fraction is lower when the Plateau border pressure is uniform. Furthermore, the surface energy is minimized if the liquid fraction is such that the (uniform) Plateau border pressure equals the outside pressure. Straight decoration of the vertices of a dry foam decreases the area of gas in the bubbles and the total surface energy. If, however, the gas area is kept fixed (by expanding the foam), then the energy may go through a minimum. Detailed results are presented for the case of wet petal clusters.


## 1. Introduction

In a two-dimensional (2D) liquid foam at equilibrium, the bubbles are bounded by liquid films which are arcs of a circle. These meet at the equilibrium angles at dry vertices in an ideal (dry) foam, or at Plateau borders (PBs) in a wet foam, as in the schematic representations of figure 1. Here we have assumed that the films have negligible thickness even in wet foams, in which all the liquid resides in the PBs.

This simplified wet foam can be regarded as a particular type of partition of the plane into regions of two types, G and L (where G denotes the gas in the bubbles, and L the liquid in the PBs), separated by two types of boundaries (or 'surfaces'): GG and GL, but not LL. An example is shown in figure 2. All vertices in such a partition are trivalent (i.e., three-connected) and are either GGG (a dry vertex) or GGL. A G region is in general bounded by GG and GL surfaces; an $L$ region is bounded by LG surfaces.

Each surface (GG or GL) has a specific free energy or tension. In an actual liquid foam the film tension $\gamma$ of the GG surfaces is usually taken as twice the bulk liquid surface tension $\gamma_{\mathrm{L}}$, i.e., the liquid-gas interfacial tension $\left(\gamma=2 \gamma_{\mathrm{L}}\right)$. This is equivalent to neglecting the
(a)
(b)


Figure 1. Films of negligible thickness meet at (a) a (dry) vertex in a dry foam or (b) a three-sided PB (shaded) in a wet foam for $\gamma=2 \gamma_{\mathrm{L}}$.


Figure 2. Partition of the plane into regions of types $G$ and $L$, as in a wet foam cluster with PBs and films of negligible thickness. This figure was drawn using the Surface Evolver for $\gamma / \gamma_{\mathrm{L}}=2$ and contains three- and four-sided PBs of different areas.
interaction between film surfaces and thus the disjoining pressure. Such an approximation is, however, consistent with assuming that films and PBs are distinct entities, with no transition region between the two. Under equilibrium the LG surfaces of the PBs then join the films tangentially, as in figure 1(b).

The equilibrium of 2D foams with G and L regions is governed by generalized Plateau rules [1] pertaining to the equilibrium of tension forces at the vertices $\left(\sum_{i} \gamma_{i}=\mathbf{0}\right)$ and of pressures across the circular films and PB surfaces. Note that the equilibrium condition $\sum_{i} \gamma_{i}=\mathbf{0}$ implies that in a wet foam $\gamma \leqslant 2 \gamma_{\mathrm{L}}$. The contractile tendency of the circular films and PB surfaces is balanced by the pressure differences $p_{i}-p_{k}=\gamma_{i k} / R_{i k}$ between adjacent regions $i$ and $k$, where $\gamma_{i k}$ and $R_{i k}$ are, respectively, the tension and the radius of curvature of the surface between regions $i$ and $k$. At any vertex where surfaces $i k$ join, the relation $\sum_{i k} \gamma_{i k} / R_{i k}=0$ holds. We concentrate on free 2D clusters which are embedded in a gas at pressure $p_{0}$, as in figure 3 . A region (gas or liquid) in the cluster has excess pressure $p_{i}^{*}=p_{i}-p_{0}$, where $p_{i}$ is the pressure in that region.

For a given topology of a 2D finite cluster embedded in a gas at pressure $p_{0}$ (see figure 3), and given areas (or excess pressures) of each of its bubbles and PBs, Plateau's laws yield a number of equations equal to the number of unknowns [2]. There may be a unique solution, but multiple solutions are of course possible [3, 4]. Furthermore, in certain area (or excess pressure) ranges there may be no solutions.

The amount of liquid in a 2 D foam can be specified by the liquid/gas area ratio, $f=A_{\mathrm{L}} / A_{\mathrm{G}}$, or by the liquid fraction $\phi_{\mathrm{L}}=A_{\mathrm{L}} /\left(A_{\mathrm{L}}+A_{\mathrm{G}}\right)$; the two are related by $\phi_{\mathrm{L}}=f /(1+f)$. The liquid content has a large effect on foam properties, in particular its ageing behaviour, its rheological properties and, of course, its surface energy [5]. The latter


Figure 3. A (2D or 3D) bubble cluster surrounded by gas at pressure $p_{0}$; only two (four-sided) PBs (shaded) are shown (angles at junctions and film radii not rendered accurately). A hollow cylinder of cross-sectional area $a$ has one end inside region 1 , of pressure $p_{1}$, and the other end outside the cluster. A force $F=a\left(p_{0}-p_{1}\right)$ must act on the piston to equilibrate the pressure difference between its two sides; in the case shown, $p_{1}>p_{0}$.
is defined as

$$
\begin{equation*}
E=L_{\mathrm{F}} \gamma+L_{\mathrm{L}} \gamma_{\mathrm{L}} \tag{1}
\end{equation*}
$$

where $L_{\mathrm{F}}$ and $L_{\mathrm{L}}$ are the total lengths of the films and of the PB surfaces, respectively.
In this paper we study various problems relating to the energy of 2D wet foam clusters at equilibrium, such as those that can be formed between two parallel horizontal plates, or between a liquid surface and a horizontal plate above it. In particular, we address the effect on the energy of the liquid fraction and of liquid partitioning among PBs, as well as the stability of clusters in relation to the excess pressures in bubbles and PBs. The paper is organized as follows. In section 2 we show that the energy is minimized as a function of the area of region $i$ when the excess pressure in that region vanishes. In section 3 we calculate the change in bubble area when the vertices of a dry cluster are decorated with PBs. In section 4 we show that the energy of a wet foam is lowest when the PB pressure is uniform. We also give rough estimates of the effect of the liquid fraction on the energy. In section 5 we solve simple wet bubble clusters that illustrate our findings, which we summarize in section 6 .

## 2. Energy and energy minima

In a 2D free foam cluster at equilibrium, the total surface energy $E$ is related to the areas $A_{i}$ of the different regions and to their excess pressures $p_{i}^{*}$ by $[6,7]$

$$
\begin{equation*}
E=2 \sum_{i} A_{i} p_{i}^{*} \tag{2}
\end{equation*}
$$

where the sum is over all regions. This equation suggests that increasing the area of region $i$ in the cluster may either raise or lower the cluster energy depending on the sign of the excess pressure $p_{i}^{*}$. To analyse this in more detail, let us consider the change in surface energy when the area of a given region (say, region 1 ) is varied, while keeping constant the areas of all other regions: $E=E\left(A_{1}\right)$. The following argument shows that when the excess pressure in that region vanishes, $p_{1}^{*}=0$, the energy $E\left(A_{1}\right)$ will be stationary. Consider a hollow cylinder fitted with a piston of diameter $a$. One of the two (open) ends of the cylinder is in region 1 and the other is in the outside gas, as in figure 3. The cylinder does not otherwise perturb the foam. Equilibrium requires the force on the piston to be $F=a\left(p_{1}-p_{0}\right)$; see figure 3. A displacement $\mathrm{d} x$ of the piston changes the area of region 1 by $\mathrm{d} A_{1}=a \mathrm{~d} x$. At equilibrium,
(a)

(d)

(b)

(e)

(c)

(f)


Figure 4. ((a), (b)) Petal bubble clusters with a central bubble of area $A_{c}$ surrounded by, respectively, $n=4$ and 7 peripheral bubbles of area $A$ each. (c) Definition of geometrical quantities pertaining to a petal cluster without a central decoration. (d) Petal cluster with a central PB: $r_{0}$ is the PB surface radius. (e) Petal cluster with peripheral PBs only: $r_{1}$ and $r_{2}$ are the PB surface radii. (f) Photograph of five-petal cluster with both central and peripheral PBs (courtesy of M F Vaz).
the work performed by the force on the piston, $\mathrm{d} W=F \mathrm{~d} x$, equals the change in (Helmholtz) surface free energy, $\mathrm{d} E$, leading to $\mathrm{d} E=p_{1}^{*} \mathrm{~d} A_{1}$. Thus, for $p_{1}^{*}=0$ the free energy is stationary (presumably a minimum, if the equilibrium is stable). The same conclusion holds for 3D foams. Note that it may not be possible for $p_{1}^{*}$ to vanish, but if it does then $\partial E / \partial A_{1}=0$. For example, in a (dry) petal cluster with $n$ bubbles of area $A$ surrounding an $n$-sided bubble of area $A_{\mathrm{c}}$ (see figures $4(\mathrm{a}),(\mathrm{b})$ ), it is not possible to have zero excess pressure $p_{\mathrm{c}}^{*}$ in the central bubble for any $A_{\mathrm{c}} / A$ if $n<6$ [8]. These petal clusters were found to be unstable when the excess pressure in the central bubble is negative and $\mathrm{d} E / \mathrm{d} A_{\mathrm{c}}<0[3,8]$, which may happen for $n>6$. However, a negative excess pressure may not be a sufficient condition for instability of a wet foam: for example, we found, using the Surface Evolver [9], that a triangular PB surrounded by three identical bubbles (similar to that in figure 4(c)) is stable for negative excess pressure of the liquid.

Since the PBs are connected by the films, the liquid in the cluster is expected to have uniform pressure $p_{\mathrm{L}}$ (excess pressure $p_{\mathrm{L}}^{*}=p_{\mathrm{L}}-p_{0}$ ); we may thus rewrite equation (2) as

$$
\begin{equation*}
E=2 \sum_{\text {bubbles }} A_{i} p_{i}^{*}+2 A_{\mathrm{L}} p_{\mathrm{L}}^{*} \text {. } \tag{3}
\end{equation*}
$$

As the liquid fraction is changed at fixed bubble areas, the energy is minimal when $p_{\mathrm{L}}^{*}=0$, i.e., when the excess pressure in the liquid vanishes.

## 3. Vertex decoration by Plateau borders

Three-sided (triangular) PBs in 2D foams are special in that they are decoration PBs, i.e., PBs to which the decoration theorem $[16,17]$ applies. This theorem states that the circular film prolongations into a three-sided PB at equilibrium meet at a single point at angles of $2 \pi / 3$. (This also applies to any other three-sided decorations, of any $\gamma_{\mathrm{D}} / \gamma \geqslant 1 / 2$, at equilibrium, where $\gamma_{D}$ is the (uniform) tension of the decoration surfaces.) Conversely, a dry triple film junction can be decorated with a PB (or some other decoration) without disturbing the films.
(a)

(c)

(b)

(d)


Figure 5. ((a) and (b)) triangular PB with mirror symmetry plane: the PB surfaces have radii $r_{1}$, $r_{1}$ and $r_{2}$ and the PB regions bounded by the PB surfaces and the film prolongations (dashed lines) have areas $A_{31}$ and $A_{32}$. (c) Regular four-sided bubble decorated with triangular PBs at its vertices (only one is shown). (d) Regular seven-sided bubble decorated with triangular PBs at its vertices (only one is shown). In (c) and (d), $R$ is the radius of the bubble films and $2 \theta$ is the angle they subtend.

The decoration property does not apply to $n$-sided PBs with $n>3$, except in special cases, such as $n$-fold symmetric regular PBs [18].

In view of the decoration theorem, an excess energy $\epsilon_{3}$ may be defined for three-sided PBs which is given by [18]

$$
\begin{equation*}
\epsilon_{3}=L_{\mathrm{PB}} \gamma_{\mathrm{L}}-L_{\text {prol }} \gamma, \tag{4}
\end{equation*}
$$

where $L_{\mathrm{PB}}$ and $L_{\text {prol }}$ are the lengths of the PB surfaces (of tension $\gamma_{\mathrm{L}}$ ) and of the film prolongations into the PBs (of tension $\gamma$ ), respectively; for 'normal' PBs ( $\gamma_{\mathrm{L}}=\gamma / 2$ ), the excess energy is negative.

We have shown [18] that the ratio $\epsilon_{3} /\left(\gamma \sqrt{A_{3}}\right)$ (where $A_{3}$ is the area of the three-sided PB) is weakly dependent on the size and shape of the PB , and takes on a value close to that for a regular three-sided PB, which for $\gamma_{\mathrm{L}}=\gamma / 2$ is

$$
\begin{equation*}
\frac{\epsilon_{3}}{\gamma}=-\left[\left(\sqrt{3}-\frac{\pi}{2}\right) A_{3}\right]^{1 / 2} \simeq-0.4016 \sqrt{A_{3}} . \tag{5}
\end{equation*}
$$

The area $A_{3}$ of a regular three-sided PB is in turn related to the radius $r$ of its surfaces by

$$
\begin{equation*}
\sqrt{A_{3}} \simeq 0.4106 r \tag{6}
\end{equation*}
$$

i.e., by the same proportionality constant as in equation (5).

In what follows we examine the partitioning of the liquid in a three-sided PB among the three bubbles that it 'invades' when a dry vertex is decorated. Our purpose is to find the change in the area of a bubble when all its vertices are decorated with (triangular) PBs. We calculate this change for regular $n$-sided bubbles, which in their dry state consist of $n$ identical circular films of radius $R$ meeting at internal angles of $2 \pi / 3$, and $n$ straight films symmetrically connected to its $n$ vertices, as illustrated in figures 5(c), (d) for $n=4$ and 7 . The area $A_{\mathrm{G}_{0}}$ of the undecorated (dry) bubble is

$$
\begin{equation*}
\frac{A_{\mathrm{G}_{0}}}{n}=R^{2}\left(\sin ^{2} \theta \cot \frac{\pi}{n}+\theta-\sin \theta \cos \theta\right), \tag{7}
\end{equation*}
$$

where

$$
\begin{equation*}
\theta=\pi\left(\frac{1}{n}-\frac{1}{6}\right) \tag{8}
\end{equation*}
$$

is the angle between the films and their chords (see figures 5(c), (d)). For $n>6$ we take $R>0$; for $n<6, R<0$; for $n=6,1 / R=0$. We decorate the $n$-vertices with triangular PBs of area $A_{3}$ each (see figures 5(c), (d) again). These PBs have a mirror symmetry plane (see figure 5(a)) and surface radii $r_{1}, r_{1}$ and $r_{2}$, in terms of which we write the PB area $A_{3}$, its excess energy $\epsilon_{3}$ and the areas of liquid $A_{31}$ and $A_{32}$ bounded by the film prolongations and the PB surfaces of radii $r_{1}$ and $r_{2}$ respectively (see figure 5(b)), with

$$
\begin{equation*}
A_{3}=2 A_{31}+A_{32} \tag{9}
\end{equation*}
$$

expressions for which are derived in the appendix.
Equilibrium of pressures requires that (when $\gamma=2 \gamma_{\mathrm{L}}$ )

$$
\begin{equation*}
\frac{1}{r_{2}}-\frac{1}{r_{1}}+\frac{2}{R}=0 . \tag{10}
\end{equation*}
$$

Equation (A.7) of the appendix gives the area $A_{3}$ of the triangular PB as a function of $r_{1}$ and $r_{2}$, and equations (A.9) and (A.10) give the area $A_{32}$ of the liquid that 'invades' the bubble. This equals the decrease in the bubble gas area due to decoration of one of its dry vertices with a PB. The bubble area after decoration with $n$ PBs is thus

$$
\begin{equation*}
A_{\mathrm{G}}=A_{\mathrm{G}_{0}}-n A_{32} \tag{11}
\end{equation*}
$$

In figure 6(a) we plot the area fraction $A_{32} / A_{3}$ versus $A_{3} / A_{\mathrm{G}}$ for several $n$ : it is an increasing function for $n>6$ and a decreasing function for $n<6$. For $n=6$, it equals $1 / 3$. Figure 6(b) shows the total area $n A_{32}$ of gas removed from a regular $n$-sided bubble due to decoration of its $n$ vertices with PBs of area $A_{3}$ each, versus $A_{3} / A_{G}$ : the dependence is nearly linear, with a coefficient of proportionality that is in turn approximately proportional to $n$. The larger $n$, the larger the fraction of gas area 'lost' on decoration of regular $n$-sided bubbles of fixed area.

Lewis's law [10-13], which approximately applies to 2D foams [14, 15], relates the average area $\langle A\rangle_{n}$ of $n$-sided bubbles in a (large) random cluster to $n$ :

$$
\begin{equation*}
\langle A\rangle_{n}=\langle A\rangle[1+c(n-6)], \tag{12}
\end{equation*}
$$

where $\langle A\rangle \equiv\langle A\rangle_{6}$ is the average bubble area and $c$ is a constant $(0<c<1 / 3)$; bubbles with more sides have larger average area and vice versa. If we now decorate all vertices of a dry random foam with PBs of area $A_{3}$ each, the average fraction of gas area removed from an 'average' regular $n$-sided bubble, $n A_{32} /\langle A\rangle_{n}$, is approximately the same for all $n$, as shown in the plot of figure 6 (c) for $c=0.25$, which is in reasonable agreement with experiment [14, 15]. Therefore on average, each bubble suffers approximately the same percentage area reduction when PBs are placed at all its vertices. We shall use this result in the following section.

## 4. Liquid partitioning and the energy of wet clusters

Starting with a dry 2D foam cluster (with threefold vertices) and given bubble areas, we can construct related wet clusters by placing triangular PBs of uniform pressure at all its vertices. This can be done without disturbing the films (cf decoration theorem [16, 18]), but the area of


Figure 6. (a) Fraction of PB area that invades a regular $n$-sided bubble, $A_{32} / A_{3}$, versus relative size of $\mathrm{PB}, A_{3} / A_{\mathrm{G}}$, where $A_{\mathrm{G}}$ is the area of gas in the bubble. (b) Area fraction of liquid inside a bubble, $n A_{32} / A_{\mathrm{G}}$, versus relative size of $\mathrm{PB}, A_{3} / A_{\mathrm{G}} ; n A_{32} / A_{3}$ is nearly independent of $A_{3} / A_{\mathrm{G}}$ and $n$. (c) $n A_{32} /\langle A\rangle_{n}$ versus relative size of $\mathrm{PB}, A_{3} /\langle A\rangle$, where $\langle A\rangle_{n}$ is the average area of an $n$-sided bubble and $\langle A\rangle=\langle A\rangle_{6}$ is the average bubble area (see equation (12)). Here $c=0.25$, for which the curves for different $n$ collapse very well onto one another.
gas in the bubbles will change. The energy of the wet cluster is

$$
\begin{equation*}
E=E_{0}+\sum_{i} \epsilon_{3 i}, \tag{13}
\end{equation*}
$$

where $E_{0}$ is the energy of the dry cluster and the sum is over all PBs , of excess energy $\epsilon_{3 i}$ each. If the pressure in the (triangular) PBs is uniform, we expect their surface curvatures to also be fairly uniform, at least when they are are much larger than the film curvatures, as is the case in a fairly dry foam. The PB areas $A_{i}$ and excess energies $\epsilon_{3 i}$ are then also fairly uniform, as discussed at the beginning of section 3 .

Uniformity of the PB areas is associated with a low cluster energy, as the following argument shows. Let $A_{\mathrm{L}}=\sum_{i} A_{i}$ be the total area of liquid in the three-sided PBs. The difference between the energies of the wet and dry cluster is $E-E_{0}=\sum_{i} \epsilon_{3 i} \approx-c_{3} \gamma \sum_{i} \sqrt{A_{i}}$ where $c_{3} \simeq 0.4016$, cf equation (5). Now if $\sum_{i} A_{i}$ is kept fixed, $\sum_{i} \sqrt{A_{i}}$ is maximal when all $A_{i}$ are identical, whence the energy is lower if all PBs have the same area (hence nearly uniform pressure).

We may replace $\sum_{i} \epsilon_{3 i}$ in equation (13) by $V \bar{\epsilon}_{3}$, where $V$ is the number of vertices (or PBs ) in the cluster and $\overline{\epsilon_{3}}$ is the average excess energy. Since $\epsilon_{3 i}$ and $A_{i}$ are fairly uniform, we may take $\overline{\epsilon_{3}}=-c_{3} \gamma \sqrt{\overline{A_{3}}}$, with $V \overline{A_{3}}=A_{\mathrm{L}}$. From equation (5) we have

$$
\begin{equation*}
\frac{E}{\gamma}=\frac{E_{0}}{\gamma}-c_{3} V \sqrt{\overline{A_{3}}}=\frac{E_{0}}{\gamma}-c_{3} \sqrt{V} \sqrt{A_{\mathrm{L}}} . \tag{14}
\end{equation*}
$$

Thus in the case where the PBs are introduced at constant total cluster area $A_{\mathrm{c}}$, the energy decreases linearly with increasing $A_{\mathrm{L}}$, i.e., with increasing liquid fraction $\phi_{\mathrm{L}}=A_{\mathrm{L}} / A_{\mathrm{c}}$.

We now turn to decoration at constant bubble gas areas, which more realistically describes the wetting of an actual foam by added liquid. The films are disturbed and the change in energy has to be calculated once the new geometry has been found. However a rough estimate of the energy change can be made. We start by uniformly magnifying the dry cluster to an area $A_{\mathrm{G}}+A_{\mathrm{L}}$, where $A_{\mathrm{G}}$ is the fixed total gas area (the area of the dry cluster) and $A_{\mathrm{L}}$ is the area of liquid to be inserted. To achieve this the original cluster area $A_{\mathrm{G}}$ is multiplied by $1+A_{\mathrm{L}} / A_{\mathrm{G}}$, hence its linear dimensions and energy are multiplied by $\left(1+A_{\mathrm{L}} / A_{\mathrm{G}}\right)^{1 / 2}$. From the conclusion drawn at the end of the preceding section it follows that, after decoration with the PBs, the area of gas in each bubble is approximately restored to its original value. The energy becomes

$$
\begin{equation*}
E=E_{0}\left(1+\frac{A_{\mathrm{L}}}{A_{\mathrm{G}}}\right)^{1 / 2}+\sum_{i} \epsilon_{3 i} \tag{15}
\end{equation*}
$$

Taking, as before, $\sum_{i} \epsilon_{3 i}=-c_{3} \gamma \sqrt{V} \sqrt{A_{\mathrm{L}}}$, we may rewrite equation (15) as

$$
\begin{equation*}
E=E_{0}\left(1+\frac{A_{\mathrm{L}}}{A_{\mathrm{G}}}\right)^{1 / 2}-c_{3} \gamma \sqrt{V} \sqrt{A_{\mathrm{L}}} \tag{16}
\end{equation*}
$$

or, dividing by $\gamma \sqrt{A_{\mathrm{G}}}$,

$$
\begin{equation*}
\frac{E}{\gamma \sqrt{A_{\mathrm{G}}}}=\frac{E_{0}}{\gamma \sqrt{A_{\mathrm{G}}}}\left(1+\frac{A_{\mathrm{L}}}{A_{\mathrm{G}}}\right)^{1 / 2}-c_{3} \sqrt{V} \sqrt{\frac{A_{\mathrm{L}}}{A_{\mathrm{G}}}} \tag{17}
\end{equation*}
$$

As $A_{\mathrm{L}} / A_{\mathrm{G}}$ increases from zero, the energy goes through a minimum at

$$
\begin{equation*}
\left(\frac{A_{\mathrm{L}}}{A_{\mathrm{G}}}\right)^{*}=\left[\frac{1}{c_{3}^{2} V}\left(\frac{E_{0}}{\gamma \sqrt{A_{\mathrm{G}}}}\right)^{2}-1\right]^{-1} \tag{18}
\end{equation*}
$$

This minimum may not be attained if it is pre-empted by PB coalescence, as in the case of a decorated regular honeycomb foam [18]. As discussed above, we expect this energy minimum to be associated with zero excess pressure in the liquid. In the next section we test equation (18) for a three-petal cluster.

## 5. Calculations of wet petal clusters

We illustrate the foregoing discussion with calculations for clusters which, when dry, consist of $n$ bubbles of equal areas ('petals') joined at an $n$-fold vertex, as in figure 4(c) for $n=7$; these dry clusters are of course not stable when $n>3$. The area $A_{0}$ of one petal bubble is related to the radius $R_{0}$ of the circular outer films by

$$
\begin{equation*}
A_{0}=R_{0}^{2}\left[\sin ^{2} \theta \cot \frac{\pi}{n}+\theta-\sin \theta \cos \theta\right], \tag{19}
\end{equation*}
$$

where

$$
\begin{equation*}
\theta=\pi\left(\frac{1}{n}+\frac{1}{6}\right) \tag{20}
\end{equation*}
$$



Figure 7. Reduced energy $E /\left(n \gamma \sqrt{A_{\mathrm{G}}}\right)$ (top) and reduced excess pressure $A_{\mathrm{G}}^{1 / 2}\left(p_{\mathrm{L}}-p_{0}\right) / \gamma$ (bottom) versus $\left[A_{\mathrm{L}} /\left(n A_{\mathrm{G}}\right)\right]^{1 / 2}$ for a petal cluster with a central PB of area $A_{\mathrm{L}}$.
is half the angle subtended by the arc of radius $R_{0}$ (see figure 4(c)). The total energy of the dry cluster is

$$
\begin{equation*}
\frac{E_{0}}{n \gamma}=2 R_{0}\left(\frac{\sin \theta}{2 \sin \frac{\pi}{n}}+\theta\right) \tag{21}
\end{equation*}
$$

The $n$-fold vertex can be decorated with a regular PB bounded by $n$ arcs of circle of radius $r$ each, as in figure 4(d). The area $A_{\mathrm{L}}$ of this central PB is

$$
\begin{equation*}
\frac{A_{\mathrm{L}}}{n}=r^{2}\left(\cot \frac{\pi}{n}+\frac{\pi}{n}-\frac{\pi}{2}\right) \tag{22}
\end{equation*}
$$

the area $A_{\mathrm{G}}$ of gas in one bubble is

$$
\begin{equation*}
A_{\mathrm{G}}=A_{0}-\frac{A_{\mathrm{L}}}{n}, \tag{23}
\end{equation*}
$$

and the PB excess energy $\epsilon_{n}$, defined as for triangular PBs as the difference between the energy of the PB surfaces and that of the film prolongations into the PB , which do indeed meet at a single point, is [18]

$$
\begin{equation*}
\frac{\epsilon_{n}}{n \gamma}=r\left(-\cot \frac{\pi}{n}+\frac{\pi}{n}-\frac{\pi}{2}\right) \tag{24}
\end{equation*}
$$

The energy $E$ of the wet cluster is

$$
\begin{equation*}
E=E_{0}+\epsilon_{n} \tag{25}
\end{equation*}
$$

In figure 7 we plot the reduced energy $E /\left(n \gamma \sqrt{A_{G}}\right)$ and the reduced excess pressure $A_{\mathrm{G}}^{1 / 2}\left(p_{\mathrm{L}}-p_{0}\right) / \gamma$ versus the liquid/gas area ratio $\left[A_{\mathrm{L}} /\left(n A_{\mathrm{G}}\right)\right]^{1 / 2}$. As predicted in section 4 , the energy has a minimum when the pressure in the PB equals the outside pressure $\left(p_{\mathrm{L}}=p_{0}\right)$.

We have also calculated a wet cluster obtained by decorating the $n$-petal dry cluster with $n$ identical peripheral PBs (see figures 4(e), (f)). These PBs have a mirror plane of symmetry


Figure 8. The same as figure 7, but for a petal cluster with $n$ peripheral PBs of total area $A_{\mathrm{L}}$.
and surface radii $r_{1}, r_{1}$ and $r_{2}$, which are related to $R_{0}$ by equation (10). $1 / R_{0}$ has the same sign as $n-6$. The required equations are derived in the appendix. Upon decoration, the area of gas in each bubble becomes

$$
\begin{equation*}
A_{\mathrm{G}}=A_{0}-2 A_{31}, \tag{26}
\end{equation*}
$$

where $A_{31}$, given by equation (A.9), is the area between the PB surface of radius $r_{1}$ and the film prolongations. The total area of liquid is $A_{\mathrm{L}}=n A_{3}$, with $A_{3}$ given by equation (A.7). The excess energy $\epsilon_{3}$ per peripheral PB is in turn given by equation (A.8); the total surface energy is

$$
\begin{equation*}
E=E_{0}+n \epsilon_{3} . \tag{27}
\end{equation*}
$$

In figure 8 we plot the reduced energy $E /\left(n \gamma \sqrt{A_{\mathrm{G}}}\right)$ and the reduced excess pressure $A_{\mathrm{G}}^{1 / 2}\left(p_{\mathrm{L}}-p_{0}\right) / \gamma$ versus $\left[A_{\mathrm{L}} /\left(n A_{\mathrm{G}}\right)\right]^{1 / 2}$ for the petal cluster with peripheral PBs. Again there is an energy minimum for $p_{\mathrm{L}}=p_{0}$.

Finally, we have calculated the wet petal cluster with central and peripheral PBs. For fixed liquid fraction $\phi_{\mathrm{L}}=A_{\mathrm{L}} / A_{\mathrm{G}}$, where $A_{\mathrm{L}}$ is the total area of liquid and $A_{\mathrm{G}}$ the area of one bubble (after decoration), we found the total energy for various $n$, which is shown in figure 9 (a) as a function of $r_{1} / r_{0}$, where $r_{0}$ and $r_{1}$ are, respectively, the radii of the central PB and of the peripheral PB surfaces within the cluster (see figures $4(\mathrm{~d})$, (e)): the pressures in the two types of PBs are the same if $r_{1} / r_{0}=1$. It is apparent that the energy minimum occurs for $r_{1} / r_{0}$ close to, but not exactly, unity, in agreement with the discussion in section 4 . The smaller the liquid fraction, the closer the energy minimum lies to the point of uniform liquid pressure; see figure $9(b)$. It is also apparent that the lowest minimum occurs at some intermediate $\phi_{\mathrm{L}}$ : for $n=3$, this is $\phi_{\mathrm{L}} \approx 0.054$, to be compared with $\phi_{\mathrm{L}} \approx 0.025$ from equation (18) with equations (19)-(21).


Figure 9. Petal cluster with one central and $n$ identical peripheral PBs. (a) Reduced energy $E /\left(n \gamma \sqrt{A_{\mathrm{G}}}\right)$ versus $r_{1} / r_{0}$ for different liquid fractions $\phi_{\mathrm{L}}$. (b) $r_{1} / r_{0}$ at the minimum of the energy versus liquid fraction $\phi_{\mathrm{L}}$; at small $\phi_{\mathrm{L}}$, the minimum occurs for nearly uniform PB pressure.

## 6. Summary

We have discussed a number of issues relating to the partitioning of liquid over the PBs of 2D bubble clusters. We used a model foam in which the films have zero thickness and are joined tangentially by the PB surfaces (i.e., $\gamma=2 \gamma_{\mathrm{L}}$ ). We have shown that the energy of a foam cluster embedded in a gas at pressure $p_{0}$ goes through a minimum as the area $A_{i}$ of the $i$ th bubble or PB is changed at constant areas of the remaining bubbles and PBs , when the excess pressure $p_{i}-p_{0}$ vanishes. We illustrated this property by performing detailed calculations of
a wet petal cluster, consisting of $n$ identical bubbles (the petals) surrounding a central $n$-sided PB , with and without peripheral PBs. Its energy goes through a minimum when the PB areas are such that the excess pressure vanishes.

When the vertices of an initially dry cluster are decorated with triangular PBs all of the same area, the area of gas in each bubble changes, but in approximately the same proportion for all bubbles, independent of the number of sides. At fixed liquid fraction, the energy of a decorated wet foam is minimal when the pressure in the PBs is nearly uniform, which is expected to be the case in actual foams, whose PBs communicate through the liquid films. We verified this for a petal cluster with central and peripheral PBs. If all PBs are triangular, (near) uniformity of pressures is equivalent to (near) uniformity of PB areas.

When a foam is wetted at fixed bubble areas, it expands in an approximately uniform manner and its surface energy (of films and PB surfaces) initially decreases, until a minimum is eventually reached. This contrasts with straight vertex decoration with PBs at fixed total cluster area, which always lowers the energy.

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We are grateful to M F Vaz for providing us with the photograph of a five-petal cluster, figure 4(f).

## Appendix. Triangular Plateau borders with a mirror plane of symmetry

The PB surfaces (of tension $\gamma_{\mathrm{L}}$ ) have radii $r_{1}, r_{1}$ and $r_{2}$ (see figure 5(a)); the radii of the two circular films (of tension $\gamma=2 \gamma_{\mathrm{L}}$ ) joining the PB is $R$ (the other film is straight). We take $r_{1}$, $r_{2}$ and $R$ to be positive as in figure 5(a); equilibrium of pressures requires

$$
\begin{equation*}
\frac{1}{r_{1}}-\frac{1}{r_{2}}-\frac{2}{R}=0 \tag{A.1}
\end{equation*}
$$

The angles subtended by the PB surfaces of radii $r_{1}$ and $r_{2}$ are, respectively, $2 \theta_{1}$ and $2 \theta_{2}$, which are related by

$$
\begin{equation*}
\theta_{1}=\frac{\pi}{2}-2 \theta_{2} \tag{A.2}
\end{equation*}
$$

The chord lengths $l_{1}$ and $l_{2}$ are given by

$$
\begin{align*}
& l_{1}=2 r_{1} \sin \theta_{1},  \tag{A.3}\\
& l_{2}=2 r_{2} \sin \theta_{2}, \tag{A.4}
\end{align*}
$$

leading to

$$
\begin{equation*}
2 \sin ^{2} \theta_{1}=\frac{1}{1+r_{1} / r_{2}} \tag{A.5}
\end{equation*}
$$

The two circles of radius $R$ are prolonged into the PB. Let $2 \alpha$ be the angle subtended by the prolongation arcs. Simple calculations yield

$$
\begin{equation*}
R \cos \left(\frac{\pi}{3}+2 \alpha\right)=\frac{R}{2}-r_{2} \sin \theta_{2} \tag{A.6}
\end{equation*}
$$

and for the area of the PB,
$A_{3}=r_{1} r_{2} \sin 2 \theta_{1} \sin \theta_{2}-2 r_{1}^{2}\left(\theta_{1}-\sin \theta_{1} \cos \theta_{1}\right)-r_{2}^{2}\left(\theta_{2}-\sin \theta_{2} \cos \theta_{2}\right)$,
and for the excess energy $\epsilon_{3}$, defined as the difference between the energy of the three PB surfaces and that of the three film prolongations (which meet at a single point),
$\frac{\epsilon_{3}}{\gamma}=2 r_{1} \theta_{1}+r_{2} \theta_{2}-\left[4 R \alpha+2 r_{1} \sin \theta_{1} \cos \theta_{1}-2 R \sin \alpha \cos \left(\frac{\pi}{3}+\alpha\right)\right]$.
The film prolongations divide the PB into three regions, each bounded by two prolongations and a PB surface. The areas of these regions, shown in figure 5, are

$$
\begin{align*}
A_{31}= & {\left[r_{1} \sin \theta_{1} \cos \theta_{1}-R \sin \alpha \cos \left(\frac{\pi}{3}+\alpha\right)\right] r_{2} \sin \theta_{2} } \\
& \quad-r_{1}^{2}\left(\theta_{1}-\sin \theta_{1} \cos \theta_{1}\right)+R^{2}(\alpha-\sin \alpha \cos \alpha),  \tag{A.9}\\
A_{32}= & A_{3}-2 A_{31} \tag{A.10}
\end{align*}
$$

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