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Shapes of Cells in Polymer Foams

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INTRODUCTION

The mechanical properties of polymer foams depend perhaps more on the geometry of the foam than on the bulk mechanical properties of the polymer itself. Of the various sorts of forces which determine the geometry of a foam, one, the surface tension, is an equilibrium effect, while viscosity is not. The problem is idealized in this paper by the neglect of the latter. With the further neglect of gravitational forces (which are readily seen to be negligible) the problem of the shape reduces to one of minimizing the surface energy, and thus of minimizing the surface area.

The distribution of position and size of the cells in a foam is something over which some control can be exercised during their formation. There is thus some arbitrariness in the sort of distribution chosen for calculation; the simplest choice, regularly spaced cells of equal size, was the one actually made. The more drastic reduction to a two-dimensional problem was also made, in order to reduce the partial differential equations which would otherwise be involved to ordinary ones.

The problem was actually solved by means of the rigorous theory based on the calculus of variations. Once the solution was at hand, however, it was seen that it could also be derived from rather simple considerations based on Laplace's equation. Since the rigorous proof is quite abstract and does not contribute to one's physical understanding, it will not be given here. It is planned to publish it elsewhere as part of a comprehensive collection of calculations of surface problems.

THE MODEL

As mentioned above, the model is to be taken as a two-dimensional one. This means that the voids will have the shape of distorted, infinitely long, cylinders, or that the general structure will be that of a honeycomb. The shape taken by such a system, under surface forces only, is such as to minimize the surface area for constant volume. For a two-dimensional model of the sort here considered, this is equivalent to minimizing the sum of the perimeters for constant area.

It is observed by microscopic or sometimes even by direct observation that generally only three cell walls intersect at a vertex. The only regular

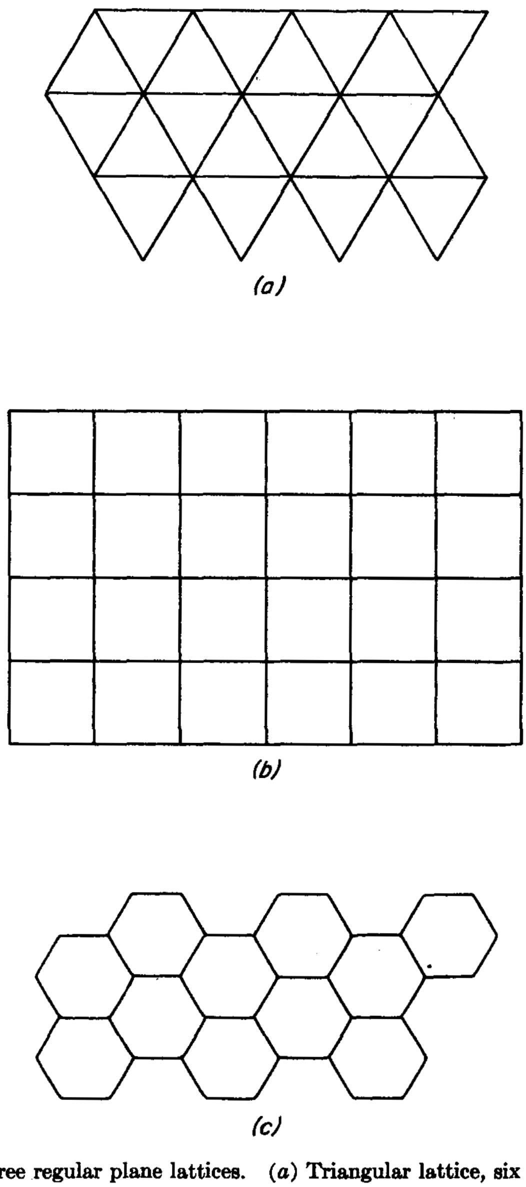

Fig. 1. The three regular plane lattices. (*a*) Triangular lattice, six walls per vertex. (*b*) Square lattice, four walls per vertex. (*c*) Hexagonal lattice, three walls per vertex.

lattice with this property is the hexagonal, as Figure 1 shows. For this reason it will be assumed that the foam is based on a hexagonal lattice.

It is also observed that the shape of the cell walls is more or less the same whether all the cells are nearly the same size or whether there is a distribution of cell sizes. For simplicity then, the limiting case of all cell sizes equal will be taken. Figure 2 shows this.

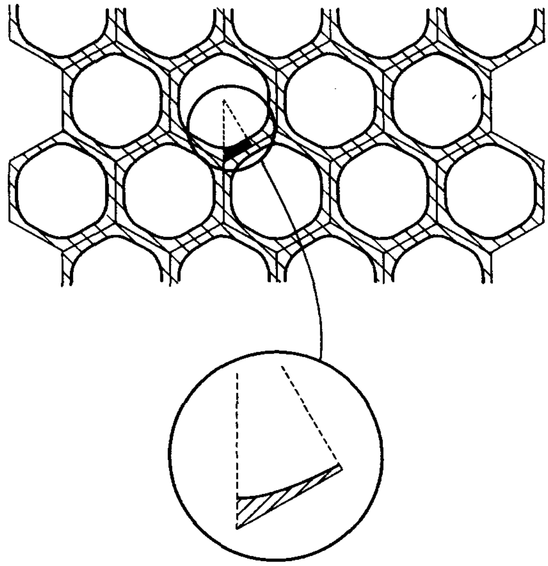

Fig. 2. Idealized model of a foam. The enlarged portion is one twelfth of a cell.

The symmetry in this model allows one to work with one twelfth of a cell, as shown in Figures 2 and 3. Symmetry also requires that the curve, as shown in Figure 3, be at right angles to the two dotted lines. For the foam as a whole (Fig. 2), the condition is that the perimeter (of all the cell walls) be a minimum subject to constant area (of the cross-hatched region). For the one twelfth of a cell the condition is of minimum length subject to constant area and also subject to crossing both dotted lines at right angles.

SOLUTION BY LAPLACE'S EQUATION

Laplace's equation is usually given in the form[1,2]

$$P_1 - P_2 = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{1}$$

where $P_1 - P_2$ is the pressure difference across the interface, γ the surface tension of the interface, and R_1 and R_2 the principal radii of curvature of the interface. The interface will be concave toward the side with greater pressure.

The dimensions of the cells are sufficiently small that the effect of gravity may be neglected, whence it is seen that the pressure difference is constant. In a general problem constancy of pressure does not in itself determine the shape, since it is only a single constraint on the two variables R_1 and R_2. However, the two-dimensional or honeycomb model assumed here implies that one of the two principal radii (say R_2) is infinite, so that the other one is thereby required to be constant

$$P_1 - P_2 = \gamma/R_1 \tag{2}$$

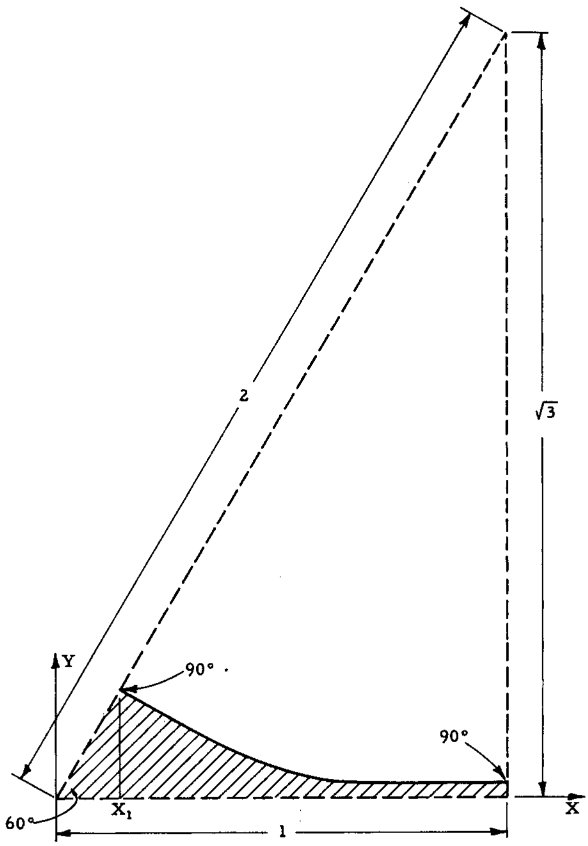

Fig. 3. One twelfth of a cell in the idealized foam model. The shape is given by the condition that the length of the curve be a minimum subject to constant area of the cross-hatched portion.

Since the circle is the only plane curve with constant radius of curvature the curve in Figure 3 must be composed of arcs of circles.

The basic parameter in a foam is the density. For the calculations it is more convenient to use the density of the foam divided by the density of bulk material, that is, the fraction of the total area in Figure 2 which is crosshatched. In what follows, unless otherwise stated, this concept will be what is denoted by "density." It is equivalent to "per cent solids by volume."

At this point some geometry is in order. Let the base of the triangle in Figure 3 be of unit length. Let the curve be given by the equation

$$Y = Y(X) \tag{3}$$

The dotted line to the left is given by

$$Y = \sqrt{3}\, X \tag{4a}$$

and that to the right by

$$X = 1 \tag{4b}$$

The area is

$$A = \int_0^{X_1} (\sqrt{3}X)dX + \int_{X_1}^{1} Y(X)dX \tag{5}$$

Since the area of the triangle is $\sqrt{3}/2$, the density is $2A/\sqrt{3}$. By a standard formula, the length of the curve is

$$L = \int_{X_1}^{1} \sqrt{1 + [Y'(X)]^2}dX \tag{6}$$

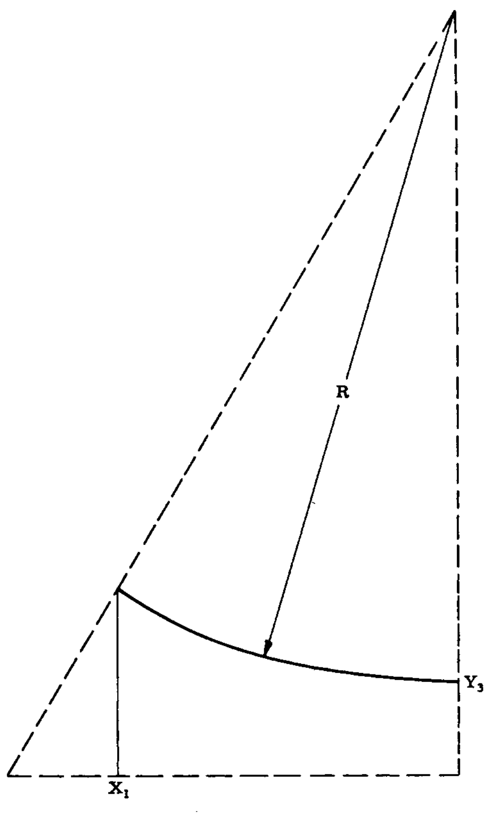

Fig. 4. A sketch of the form of the solution for $d > d_0$. The parameters are R, X_1, and Y_3.

The conditions on $Y(X)$, dictated by the fact that the triangle is only a tiny fraction of the whole structure, are that it be positive and that it cross the two dotted lines [eqs. (4a) and (4b)] at right angles. The shape of the curve is given by the requirement that the length be a minimum at constant area. All this may be summarized by $Y(X)$ such that

$$L = \text{minimum} \tag{7a}$$

$$A = \text{constant} \tag{7b}$$

$$0 \leq Y(X) \tag{7c}$$

$$Y'(X_1) = -1/\sqrt{3} \tag{7d}$$

$$Y'(1) = 0 \tag{7e}$$

If A is sufficiently large, it is possible to draw an arc of a circle centered at the apex of the triangle which will satisfy all the conditions of eqs. (2) and (7c–e). Figure 4 shows this. If the radius is R, the area of the segment of the circle is $(1/12)\pi R^2$ and the density

$$d = \frac{2}{\sqrt{3}}\left(\frac{\sqrt{3}}{2} - \frac{1}{12}\pi R^2\right) \tag{8}$$

Clearly this is the solution up to $R = \sqrt{3}$, at which point the density becomes

$$\begin{aligned} d_0 &= \frac{2}{\sqrt{3}}\left(\frac{\sqrt{3}}{2} - \frac{3\pi}{12}\right) \\ &= \left(1 - \frac{\sqrt{3}\pi}{6}\right) \\ &= 9.31\% \end{aligned} \tag{9}$$

For density of less than 9%, a circle can still be draw, but it violates condition (7c). Some idea of the form of the solution can be gotten by considering the case of $d \ll 0.09$, that is, nearly zero density, as shown in Figure 5. It is obvious that the shortest path here will be nearly a straight line, as shown, with a jog at the left to satisfy condition (7d). Though Laplace's equation is not strictly valid for $d < 0.09$, since its use leads to a solution which violates condition (7c), one may still attempt to use it at the left-hand end where (7c) is least likely to be violated. In that case the solution would consist of a circular arc at the left and a portion of the X-axis to the right. Condition (7d) requires that the center of the circle be on the line $Y = 2X$, and physically it is evident that the circle must be tangent to the X-axis. Then if the point of tangency be denoted by X_2, the center of the circle is at $X = X_2$, $Y = \sqrt{3}X_2$, the radius of the circle is $\sqrt{3}X_2$, and since $2(X_2 - X_1) = \sqrt{3}X_2$

$$\begin{aligned} X_1 &= \left(1 - \frac{\sqrt{3}}{2}\right) X_2 \\ &= 0.134X_2 \end{aligned} \tag{10}$$

By comparison with eq. (9), the area under the curve is

$$A = \left(\frac{\sqrt{3}}{2} - \frac{3\pi}{12}\right) X_2^2 \tag{11a}$$

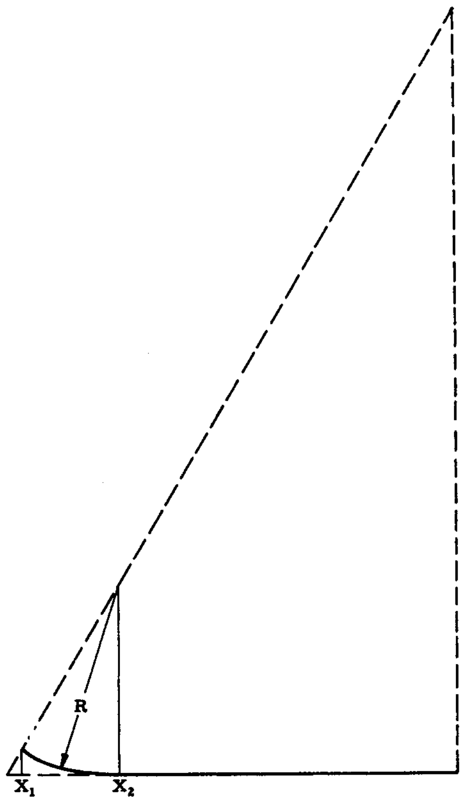

Fig. 5. A sketch of the form of the solution for $d < d_0$. The parameters are R, X_1, and X_3.

and the density

$$d = \left(1 - \frac{\sqrt{3}\pi}{6}\right) X_2^2 \tag{12a}$$

The above results may be summarized as follows: The independent parameter is the density. There are high and low density forms of the solution separated by a critical density

$$d_0 = 1 - \frac{\pi}{2\sqrt{3}} = 9.31\% \tag{13}$$

The most important dependent parameter is the radius of curvature R, given by

$$R = \sqrt{\frac{6\sqrt{3}}{\pi}}\sqrt{1-d} = 1.82\sqrt{1-d} \qquad \text{for } d \geq d_0 \tag{14a}$$

and

$$R = \sqrt{\frac{3}{1 - \frac{\pi}{\sqrt{12}}}} \sqrt{d} = 5.68 \sqrt{d} \qquad \text{for } d \leq d_0 \tag{14b}$$

A plot of R vs. d is given in Figure 6.

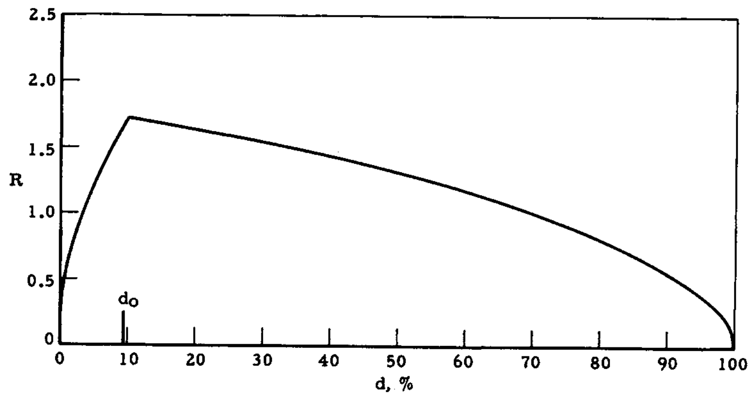

Fig. 6. Plot of radius of curvature R vs. density d.

The remaining dependent parameters, as defined above and in Figures 4 and 5, are:

$$X_1 = 1 - R/2 \tag{15a}$$

$$Y_3 = \sqrt{3} - R \tag{15b}$$

for $d \geq d_0$, and

$$X_2 = R/\sqrt{3} \tag{15c}$$

$$X_1 = X_2 - R/2 = \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right) R \tag{15d}$$

for $d \leq d_0$.

These formulas complete the formal solution of the variational problem. The derivation as given above is not completely rigorous in the mathematical sense, especially the part preceding eq. (10). However, as mentioned above, a mathematical derivation based on the calculus of variations does exist, so that one may have confidence in the results.

DISCUSSION

The detailed application of the above calculations to real foams is beyond the scope of this paper. The extent to which the two-dimensional model simulates a real foam may be seen from Figures 7 and 8. The first is a photomicrograph of Styrofoam 22, which is a large cell uniform polystyrene

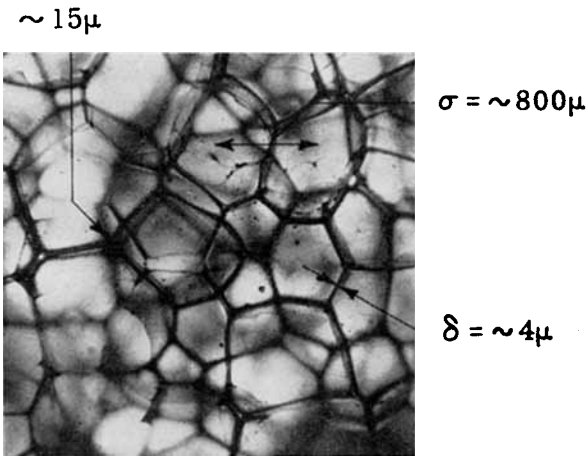

Fig. 7. Styrofoam 22, about 3% solid. 16×.

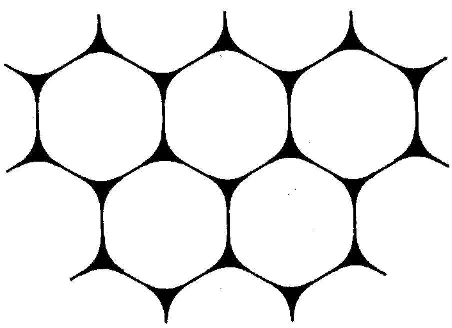

Fig. 8. Solution of the two-dimensional problem for $d = 3\%$.

foam, with a "density" of about 3% solids by volume. The second is a sketch of the solution to the two-dimensional problem for $d = 3\%$.

The combination of Laplace's equation [eq. (1)] with eq. (14) (and Fig. 6) can be used to give a qualitative picture of the process of foaming. For density nearly unity, and thereby small radius of curvature R, the equilibrium pressure is high, so that a nucleating agent is needed to help the bubble form. However, once the bubble exists a runaway situation develops, since with decrease in density the pressure necessary for surface equilibrium also decreases. This decrease in equilibrium pressure continues until the critical density d_0 is reached, at which point it reverses and begins to increase.

For densities lower than the critical density the equilibrium solution contains flat segments of zero thickness. In actual foams there are thin, nearly flat segments. By Laplace's equation the pressure difference between polymer and gas must be low for these flat segments, while it must grow increasingly great for decreasing density in the sharply curved regions. Thus the polymer in the cell faces must be at a higher pressure than in the vertices, and it is this pressure difference which leads to flow from the walls to the vertices and to thinning of the walls.

The increase in equilibrium pressure with decreasing density means that a point of balance can be reached at which the equilibrium pressure has grown as large as the pressure due to the foaming agent. This is not truly a point of equilibrium, but can be close to one insofar as the viscosity is high and cell wall thinning is a slow process.

Although the model on which these considerations are based is a two-dimensional one, it is clear that the conclusions which are drawn will be at least qualitatively correct for three-dimensional foams. There must be a critical density in three dimensions, and in fact at a greater density than 9.31%. Thus, the above discussion is valid also for real, three-dimensional foams.

References

1. Adam, N. K., *The Physics and Chemistry of Surfaces*, Oxford, 1941, p. 9.
2. Adamson, A. W., *Physical Chemistry of Surfaces*, Interscience, New York, 1960.

Synopsis

The shape of the cells in a foam is thought to be determined by the interplay between viscosity and surface tension. In order to assess the relative importance of the two, a simplified model is set up which considers only surface tension. It is assumed that the cells are of uniform cross section in one direction and are based on a regular hexagonal lattice in the other two. The resulting two-dimensional problem is solved by means of the calculus of variations. For high density foams the voids take the form of circles centered within each hexagonal cell. For low densities (below about 9% solids) the solid part is concentrated at the vertices, between tangential circular areas, connected by straight segments of zero thickness. This illustrates the importance of viscosity, since in real foams the cell walls will break if too thin, while the thinner the walls become, the greater is the effect of viscosity in opposing further thinning.

Résumé

On croit que la forme des alvéoles dans une mousse est déterminée par une compétition entre la viscosité et la tension superficielle. En vue de fixer l'importance relative de ces deux facteurs, on construitun modèle simplifié qui ne tient compte que de la tension supperficielle. On y suppose que les alvéoles possèdent une section transversale uniforme dans une des directions et sont construites suivant un réseau hexagonal régulier dans les deux autres. Le problème bidimensionnel qui en résulte est résolu par le calcul des variations. Pour des mousses de haute densité; les vides prennent la forme de cercles concentriques à chaque alvéole hexagonale. Pour des mousses de faible densité (moins de 9% de solide), la partie solide est concentrée aux sommets, entre des surfaces circulaires tangentielles, reliéa par des segments droits d'épaisseur nulle. On illustre l'importance de la viscosité, puisque dans les mousses réelles les parois de l'alvéole devraient se casser si elles étaient trop minces, tandis que, au plus minces sont les parois, au plus grand est l'effet de la viscosité qui s'oppose à un amincissement ultérieur.

Zusammenfassung

Die Gestalt der Zellen in einem Schaum ist durch das Widerspiel zwischen Viskosität und Oberflächenspannung bestimmt. Um die relative Bedeutung der beiden Grössen abzuschätzen, wird ein einfaches Modell verwendet, das nur die Oberflächenspannung in Betracht zieht. Es wird angeonmmen, dass die Zellen in einer Richtung einheitlichen Querschnitt besitzen und in den andern beiden ein regelmässiges hexagonales Gitter bilden. Das sich ergebende zweidimensionale Problem wird durch Variationsrechnung gelöst. Bei Schäumen hoher Dichte nehmen die Leerstellen die Gestalt von Kreisen an die in jeder hexagonalen Zelle zentriert sind. Bei niedriger Dichte (unterhalb 9% Festkörper) ist der feste Anteil an der Spitze, zwischen sich berührenden Kreisflächen, durch gerade Segmente der Dicke Null verbunden, konzentriert. Dadurch wird die Bedeutung der Viskosität beleuchtet, da in wirklichen Schäumen die Zellwände brechen werden, sobald sie zu dünn sind, während der Einfluss der Viskosität zur Verhinderung eines weiteren Dünnerwerdens um so grösser ist, je dünner die Wände werden.

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