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LETTER TO THE EDITOR

The conductivity of a foam

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Abstract. We present a new analysis of the dependence of electrical conductivity on liquid fraction for a foam. Ignoring the contribution of the films to both the liquid content and the conductivity, we consider only the network of liquid-filled Plateau borders and the junctions at which they meet. The effect of the junctions is calculated in the form of a vertex correction to both the conductivity and liquid fraction of the network. The correction is sufficient to account for the deviation from the linear formula of Lemlich for liquid fractions up to about 10%.

In this letter we present a significant refinement of previous theories of foam conductivity, by making allowance in a systematic way for the effects of Plateau border junctions. Our original motivation lay in the calibration of electrical conductance as a convenient method for monitoring the density (or liquid fraction) of a foam (Lemlich 1977, Peters 1995, Weaire *et al* 1995). Currently this is being used to test theories of foam drainage in vertical columns (Peters 1995, Verbist and Weaire 1994).

The dependence of resistivity on liquid fraction (or solid fraction for a conducting solid foam) is not obvious. We are, in general, faced by a disordered structure of thin films meeting at Plateau borders. Nevertheless, there is an elementary theoretical analysis, due primarily to Lemlich (1977), which relates the foam conductivity, σ_f, to the volume liquid fraction ϕ_l. The conductivity expressed relative to the value σ_l for the liquid is given by the elegant approximation

$$\sigma \equiv \frac{\sigma_f}{\sigma_l} = \frac{1}{3}\phi_l. \tag{1}$$

This is based upon neglect of current which passes through liquid films, so that the system reduces to a network of Plateau borders of the type shown in figure 1.

We will extend the argument of Lemlich to derive a nonlinear relation which is more accurate at higher values of ϕ_l. We present experimental data which are consistent with the new formula up to liquid fractions of the order of 0.1. The nonlinearity arises from the swelling of the junctions at which the Plateau borders are joined.

The development of this correction to the theory is quite elementary, but it requires the accurate calculation of some geometrical constants, which we have undertaken.

The classic analysis of Lemlich rests on a number of reasonable approximations, in addition to discounting the contribution of the liquid films. The geometry of the remaining Plateau border network is simplified as follows. The model is one of *straight* borders of *uniform* cross-section, *isotropic* (uniformly distributed in orientation) and meeting at *symmetric tetrahedral* vertices. No real foam conforms entirely to this description, but these are good approximations for many typical samples. It is further assumed that the

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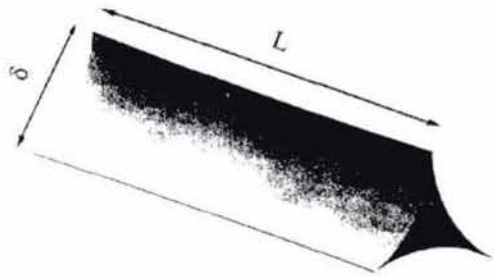

Figure 1. A section of a uniform Plateau border of length L and width δ. In general δ is defined in terms of the Plateau border pressure, P_{pb}, by $\delta = -\sigma_s/P_{pb}$ where σ_s is the surface tension and P_{pb} is negative (measured relative to the gas pressure). Here we will take $\sigma_s = 1$.

width of the Plateau borders is small compared with their length, so that there are no end corrections.

These judicious idealizations of the network structure reduce it to a form in which its conductivity is given by the Lemlich formula (1), according to arguments which we reproduce and extend below.

The Lemlich formula should be useful for low values of ϕ_l, i.e. in the dry-foam limit. Previous and subsequent experiments confirmed its validity in this limit (see e.g. Clarke 1948, Chang and Lemlich 1980, Datye and Lemlich 1983).

Not surprisingly, a considerable departure from linearity is observed as ϕ_l is increased towards its extreme value for a stable foam, which is around 0.35. *A priori*, this might be attributed to any of several effects associated with the breakdown of the approximations stated above. Indeed, the topological structure itself changes, the junctions merging to form higher-order vertices in the network as the wet limit is approached. Although full simulations will soon be possible, a transparent theory is unlikely to emerge quickly from these. Here we isolate a single correction to the elementary theory, and find it to be adequate for data in the range $0 < \phi_l < 0.08$.

The correction centres on the properties of the tetrahedral junction of Plateau borders, which is shown in figure 2. This is a surface of constant mean curvature with four symmetric arms forming Plateau borders. We are concerned with its contributions to both the *volume of liquid* and the *conductance* of the network of which it is part. These may be expressed as follows.

Let the Plateau borders have an asymptotic width δ, which is also the radius of curvature in their cross-section, and the radius associated with mean curvature over the entire surface (figures 1 and 2). The cross-sectional area is

$$A_{pb} = c_g \delta^2 \tag{2}$$

where $c_g = (\sqrt{3} - \frac{\pi}{2})$.

In Lemlich's model, each border of length L contributes to the total liquid volume the amount

$$V_{pb} = A_{pb} L. \tag{3}$$

The effect of each junction is to contribute an additional volume of the order of δ^3. We may think of this as changing the effective length of each adjoining border from L to

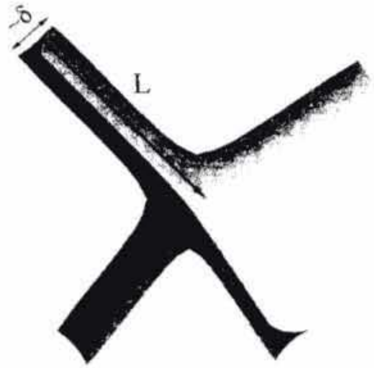

Figure 2. A single vertex and its four Plateau border arms modelled using the Evolver. In the limit of large L (measured from the centre of the vertex) the width of the arms tends to δ.

L_{eff}, retaining equation (3). There are, of course, various other ways of representing this correction.

The surface shown in figure 2 was constructed using the Surface Evolver (Brakke 1991) and its volume was calculated for various lengths of the attached arms. The results shown in figure 3 indicate that the volume correction may be represented by

$$L^{v}_{eff} = L + 0.75\delta \qquad (4)$$

as a correction to the lengths of the attached arms. However, each Plateau border in the network is attached to *two* vertices, hence

$$L^{v}_{eff} = L + 1.50\delta \qquad (5)$$

in this case.

We can perform another computation to estimate the length correction in the electrical resistance of a single Plateau border. Since the Surface Evolver creates a tessellated surface, it is ideal for the application of a boundary integral technique (Bonnet 1995) to calculate the resistance of the object shown in figure 2. This involves setting the electric potential, u, at the ends of the borders to appropriate values (two positive and two negative for example) and solving Laplace's equation, $\nabla^2 u = 0$, for the potential throughout the vertex. We need to calculate the current flow across the ends of the Plateau border arms, which is directly related to the normal derivative of u at these end surfaces. If x and y label points on the surface S, and $q(y)$ is the normal derivative of u at y, i.e. the derivative in the direction normal to S at y, then the following holds for each point x:

$$\int_S \{[u(x) - u(y)]H(x, y) - q(y)G(x, y)\}\mathrm{d}S_y = 0 \qquad (6)$$

where the Green function $G(x, y) = \frac{1}{4\pi r}$, $H(x, y) = -(1/4\pi r^3)\boldsymbol{r}\cdot\boldsymbol{n}$, $\boldsymbol{r} = \boldsymbol{y} - \boldsymbol{x}$ and $\boldsymbol{n}$ is the unit normal vector.

For a triangulated boundary of n elements we have a total of $2n$ values of q and u. Of these, n are fixed by the boundary conditions, namely, $u =$ constant at the exposed ends of the Plateau border arms and $q = 0$ on the rest of the surface. Treating u and q as constant

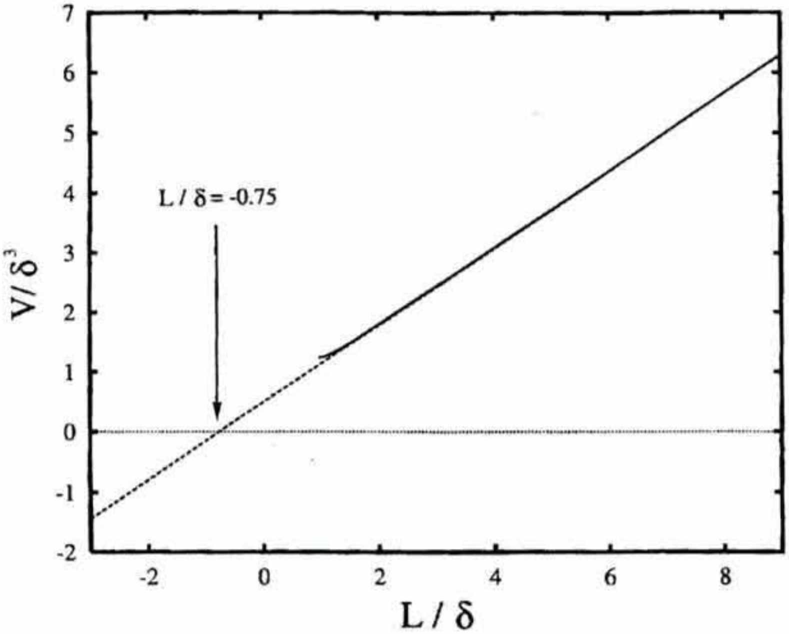

Figure 3. The relationship between the volume of a single vertex, V, the arm length, L, and δ (see figure 2). The solid curve indicates the results of Evolver calculations and the dashed line the approximate form used in the analysis presented here. The slope of this line is $4c_g \approx 0.64$ since the vertex has *four* attached arms. The magnitude of the vertex correction is indicated by the arrow.

over each individual triangle, (6) reduces to a set of n linear equations which can be solved using elementary numerical methods for the unknown potentials and normal derivatives. Integrating the values of q at the border ends gives the current and hence the resistance.

Using this method on a vertex whose surface is tessellated with 3584 triangles, we have obtained the results shown in figure 4, and hence (including the factor of two, as we did in equation (5))

$$L^{p}_{eff} = L - 1.27\delta. \tag{7}$$

We are now ready to retrace Lemlich's derivation, incorporating these corrections. It is necessary to make a further approximation, which treats the length L of all Plateau borders as equal, in order to calculate network conductance. In reality this is strictly correct only for highly ordered foam structures, but it seems reasonable to use a constant average value of L for foams which are not highly polydisperse.

Equations (5) and (7), suitably interpreted, suffice to correct Lemlich's theory for the effects of the vertices to lowest order. In the absence of vertices the volume of each Plateau border in the structure would be simply

$$V_{pb} = Lc_g\delta^2 \tag{8}$$

where c_g is the geometric constant defined in equation (2) above. Including the vertex correction this becomes

$$V_{pb} = c_g\delta^2(L + 1.50\delta). \tag{9}$$

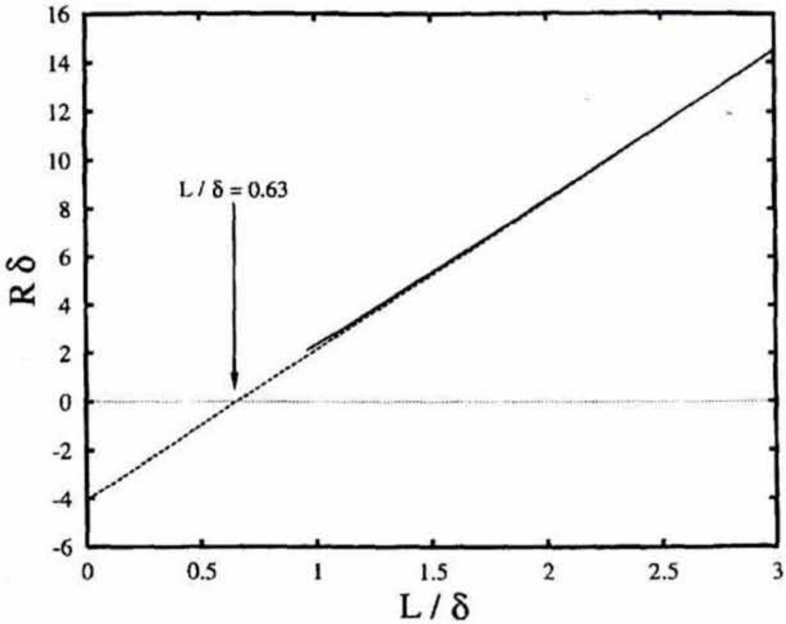

Figure 4. The relationship between the resistance of a single vertex, R, the arm length, L, and δ. The solid line shows results calculated using a boundary integral technique, the dashed line is the linear approximation with the corresponding vertex correction indicated by the arrow.

Hence if N_v is the number of borders per unit volume of the network then the liquid fraction ϕ_l is simply $N_v V_{pb}$. Equivalently if L_v is the total line length per unit volume then clearly $N_v = \frac{L_v}{L}$ and ϕ_l can be written as

$$\phi_l = L_v c_g \delta^2 (1 + 1.50\frac{\delta}{L}). \tag{10}$$

To derive the equivalent expression for the conductivity, it is convenient to examine first the dependence of resistance on L and δ. For a single uniform border of length L and width δ (figure 1, at the start of this section), the resistance is

$$R_{pb} = \frac{\rho_l L}{c_g \delta^2} \tag{11}$$

where ρ_l is the resistivity of the bulk liquid. The vertex term corrects this to

$$R_{pb} = \frac{\rho_l}{c_g \delta^2}(L - 1.27\delta) \tag{12}$$

or, in terms of conductance C_{pb},

$$C_{pb} = \frac{\sigma_l c_g \delta^2}{(L - 1.27\delta)}. \tag{13}$$

It now remains to relate the conductivity of the network to the conductance of its components, in the manner of Lemlich (1977). It is clear that at this point we may treat the borders as if they were uniform, with the above effective conductance, C_{pb}.

Kirchoff's laws are then satisfied very simply for the idealized network if the electric potential Φ is a function of one coordinate z only, i.e. $\Phi = -Ez$.

Assuming that the conductivity is isotropic, Plateau borders at an angle θ to the z direction contribute

$$\Delta j = C_{pb} E L L_v \cos^2(\theta) \tag{14}$$

to the current density j, where L_v is the line length per unit volume as before. Hence taking the spherical average over all possible orientations relative to the field we find

$$j = \frac{1}{3} C_{pb} E L L_v \tag{15}$$

or

$$j = \sigma_f E \tag{16}$$

where the foam conductivity is

$$\sigma_f = \frac{1}{3} \frac{L_v c_g \delta^2 \sigma_l}{(1 - 1.27\frac{\delta}{L})}$$

and hence, in terms of relative conductivity,

$$\sigma = \frac{1}{3} \frac{L_v c_g \delta^2}{(1 - 1.27\frac{\delta}{L})}. \tag{17}$$

Equations (10) and (17) together express the required relationship between σ and ϕ_l in a parametric form. This relationship is plotted in figure 5 where we have taken values for L_v and L corresponding to a bulk Kelvin structure. Note also that this relationship is scale independent.

Alternatively, since (17) can be rewritten as a quadratic for δ it can be solved to give

$$\delta(\sigma) = \frac{\sqrt{(\frac{1.27\sigma}{L})^2 + \frac{4}{3} L_v c_g \sigma} - \frac{1.27\sigma}{L}}{\frac{2}{3} L_v c_g}. \tag{18}$$

Combining this with (10) yields a somewhat cumbersome expression for ϕ_l in terms of σ, equivalent to (10) and (17),

$$\phi_l = L_v c_g \left(\frac{\sqrt{(\frac{1.27\sigma}{L})^2 + \frac{4}{3} L_v c_g \sigma} - \frac{1.27\sigma}{L}}{\frac{2}{3} L_v c_g} \right)^2 \times \left[1 + \frac{1.50}{L} \left(\frac{\sqrt{(\frac{1.27\sigma}{L})^2 + \frac{4}{3} L_v c_g \sigma} - \frac{1.27\sigma}{L}}{\frac{2}{3} L_v c_g} \right) \right]. \tag{19}$$

We have considered various low-order expansions of this but have not found these useful.

In considering the comparison of theory and experiment in figure 5, it should be recalled that there are no arbitrary constants in either and that the curve shown depends only on the structural parameters L_v and L taken here for the Kelvin structure. The experimental data are those of Peters (1995); for details of the apparatus see also the article by Hutzler *et al* (1995). The data of Datye and Lemlich (1983) and Chang and Lemlich (1980) are similar.

The agreement seems satisfactory up to a liquid fraction of about 0.08. Beyond this point there are corrections to the linear approximations of equations (5) and (7), and one must

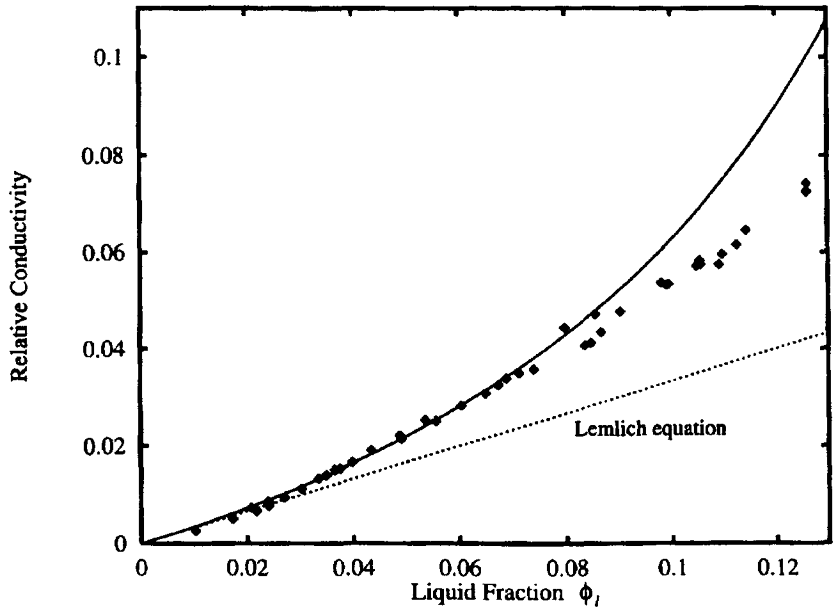

Figure 5. Experimental measurements of the relative conductivity of an aqueous foam, consisting of 3 mm bubbles in a Perspex cylinder of diameter 2 cm and height 70 cm. The solution used was ordinary tap water and a non-ionic surfactant (dobanol). The dashed line is the Lemlich limit $\sigma \equiv \sigma_f/\sigma_l = \frac{1}{3}\phi_l$. The solid curve shows the relationship based on equations (10) and (17) which include the vertex corrections.

also bear in mind the thickening of the films and their consequent increasing contribution to σ.

Note that, with the benefit of hindsight, the neglect of the junctions in the Lemlich theory looks quite naive: both (10) and (17) incorporate large corrections. For example, at a liquid fraction of 0.05 there is approximately a 100% correction to both ϕ_l and σ but only a 30% difference between the Lemlich limit and $\sigma(\phi_l)$ shown in figure 5.

In future work we intend to pursue the nonlinearity to higher values of liquid fraction, particularly the role of the films. In the earlier experimental work of Datye and Lemlich (1983), some dependence of σ on bubble size was noted which is probably indicative of the contribution of the films.

This theory should also be relevant to other transport properties, particularly heat conduction in solid foams. With some modification it may also apply to drainage in liquid foams. It will be interesting to see whether the same sort of cancellation applies in the fluid dynamics of the Plateau border network. Theories of foam drainage (Verbist and Weaire 1994) have been based on assumptions analogous to those of Lemlich. They have proved quite successful but now need to be re-evaluated. The general approach which we have developed may be applied to other foam properties as well, in each case narrowing the gap between highly idealized models and realistic structures.

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References

Bonnet M 1995 *Équations Intégrales et Éléments de Frontière* (Paris: CNRS–Eyrolles)
Brakke K 1992 *Exp. Math.* **1** 141
Chang K-S and Lemlich R 1980 *J. Colloid Interface Sci.* **73** 224
Clarke N O 1948 *Trans. Faraday Soc.* **44** 13
Datye A K and Lemlich R 1983 *Int. J. Multiphase Flow* **9** 627
Hutzler S, Verbist G, Weaire D and van der Steen J A 1995 *Europhys. Lett.* **31** 497
Lemlich R 1977 *J. Colloid Interface Sci.* **64** 107
Peters E A J F 1995 *MSc Thesis*
Verbist G and Weaire D 1994 *Europhys. Lett.* **26** 631
Weaire D, Findlay S and Verbist G 1995 *J. Phys.: Condens. Matter* **7** L217