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The impedance of a self-affine surface

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Abstract. A family of self-affine surfaces is used to model the interface between a rough blocking electrode and an electrolyte. It is shown that the surface impedance scales as $(i\omega)^{-p}$ where the exponent p varies from 0 to 1. An expression for p is found in terms of the surface geometry. It is shown that p depends on both the Holder exponent, H, and the degree of sparseness of the structure. For surfaces whose structure is everywhere dense, or very sparse, this anomalous power-law behaviour is no longer seen.

1. Introduction

When an electrolyte is in contact with a smooth blocking electrode, the interface between them prevents the passage of ionic current. Under an AC voltage the interface behaves like a capacitance. The system can be modelled by the equivalent circuit of a surface impedance Z_s, equal to $1/i\omega C$ where C is the surface capacitance, in series with a bulk electrolyte impedance Z_e. Z_e is usually a resistance. The total impedance can be written as

$$Z(\omega) = Z_e + 1/i\omega C. \tag{1}$$

However, as early as 1926 [1] an anomalous frequency dependence was discovered if the contact between the electrode and a solid electrolyte was rough. The impedance was given by

$$Z(\omega) = Z_e + K(1/i\omega)^p \tag{2}$$

where $0 < p \leqslant 1$ and ω is the angular frequency of the AC signal.

This constant phase angle (CPA) dependence has been verified by a large number of subsequent workers: de Levie rediscovered this behaviour in 1963 [2] and later work on a range of solid electrolyte systems was performed by Bottelberghs and Broers [3] and Armstrong and Burnham [4]. Most recent studies have been carried out by Bates *et al* [5, 6], who also looked at liquid electrolytes. Descriptions and reviews of further work can be found in [7-10]. The experiments are very easily and accurately performed, and equation (2) was found to hold in many systems for up to 5 decades of frequency [3-6], with p varying from 0.39-0.98. Armstrong and Burnham realised that this was due to the roughness of the boundary and that p would depend on its geometry. They measured the impedance of β-alumina in contact with a gold electrode. They found that p decreased the rougher the electrode. When it was polished, p

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approached 1. Since a power-law impedance is observed, it was reasonable to suggest that this could be derived from a fractal boundary with p related to the fractal dimension. This was done by Liu [11] and extended by Kaplan and Gray [12, 13], who described the contact as an arrangement of parallel grooves. Halsey [14] considered the interface as a supposition of mountains and valleys of different sizes. Other theoretical approaches include the simple scaling arguments used by Nyikos and Pajkossy [15], which, unfortunately, produced results which were inconsistent with other treatments of the problem, while Sapoval has studied the behaviour of porous surfaces [16], Clerc *et al* [17] have modelled the experimental systems as Sierpinski gaskets, and Keddam and Takenouti [18] have calculated the impedance of a Koch curve.

In [19] a renormalisation scheme is used to study the impedance of a large self-similar surface in contact with an electrolyte of low conductivity. However, in some recent experiments Bates *et al* [6] have studied a highly conducting liquid electrolyte, 0.1 M sulphuric acid, in contact with an electrode which was rough on scales less than 1 μm. The geometry of the electrodes was characterised as self-affine.

In this paper we shall calculate the impedance of a family of self-affine surfaces, which represent a generalisation of the model introduced by Liu [11]. For surfaces where the structure is not everywhere dense we find CPA behaviour and obtain an analytical expression for p. However, there is no direct relationship between p and other scaling exponents describing the geometry. This is in agreement with the conclusion of [6]. For surfaces with dense structure, or with very sparse features, we no longer see an anomalous power-law impedance.

2. Self-affine geometries

Self-similar fractals are dilationally invariant. That is, a piece of the fractal resembles the whole, regardless of its orientation in space—it contains overhangs and features orientated in all directions. Other curves or surfaces may have structure over a wide range of length, but with the features aligned along a particular direction. They may be described by a single-valued height function $h(x)$. The function is statistically invariant under the rescaling of axes $x \to cx$ and $h \to c^H h$, for arbitrary c between upper and lower cutoffs. The Holder exponent, H, is an exponent describing the scaling properties of the curve and lies between 0 and 1. Such objects have a self-affine geometry [20]. The description can also be extended to patterns whose boundary is not necessarily single-valued, but which are invariant under the rescaling of axes given above. We shall not be concerned explicitly with such cases here.

Imagine that we attempted to measure the arc length of such a curve with small yardsticks of length e. A unit range of x would be covered with $1/e$ such sticks. However, in each increment of size e, we expect typically a displacement h of order e^H. Hence the length of the curve, summed over $1/e$ such displacements, scales as e^{H-1}. The dimension d_H of the interface is defined such that the apparent arc length scales as e^{-d_H+1} [20]. Hence

$$d_H = 2 - H. \tag{3}$$

This is the dimension of the interface and not a quantity defined on an external border of the structure. Smooth curves have H and d_H both equal to 1.

Another statistical measure of H comes from the function $S(\Delta)$:

$$S(\Delta) = \langle (h(x+\Delta) - h(x))^2 \rangle \tag{4}$$

where we average over x. Since on a self-affine curve an increment Δ in x represents a displacement Δ^H in h, we find

$$S(\Delta) \sim \Delta^{d_\Delta} \tag{5}$$

where d_Δ equals $2H$.

Bates *et al* [6] measured the height of the electrode surface with a 0.5 μm diameter diamond stylus, which resolved structure of size 0.04-1.0 μm. The surface had been roughened by polishing with emery paper and alumina powder of varying grit size. $S(\Delta)$ was then measured and the results were consistent with a self-affine surface, with H close to 1 for the variety of electrodes studied. The surface impedance was then measured and values of p in the power law (2) were found in the range 0.78-0.97. However, no relation was found between the value of p and the exponent H.

Liu [11] proposed a model of a rough surface for which he was able to calculate the surface impedance. A generalisation of the structure is shown in figure 1(a). The surface is imagined as a succession of rectangular grooves: at the base of each groove lie b others of a width m times smaller. Figure 1(a) illustrates the case $b=2$ and $m=4$. A surface is generated by extending the system of grooves in a plane perpendicular to the paper. The structure is self-affine with an exponent H. If the whole surface has a unit width, then at the jth level of structure there are b^j grooves of width m^{-j} and height m^{-jH}. For large j they will be much narrower than they are tall. In the figure only three hierarchies of grooving are shown; the model, in general, will be generated from a total of n iterations, where n may be large. Notice that, at each stage, large portions of the surface are completely flat. The surface is not everywhere rough.

We can find d_H and $S(\Delta)$ directly. The total arc length of the cross section of the surface will be dominated by the vertical sections. For the grooves at the jth stage, this length will be of the order $m^{-jH}b^j$. This is largest for the furthest stage of iteration which can be resolved. Thus for a probe seeing n stages, the size of the probe, e, is m^{-n} and we obtain

$$d_H = 1 - H + \ln(b)/\ln(m). \tag{6}$$

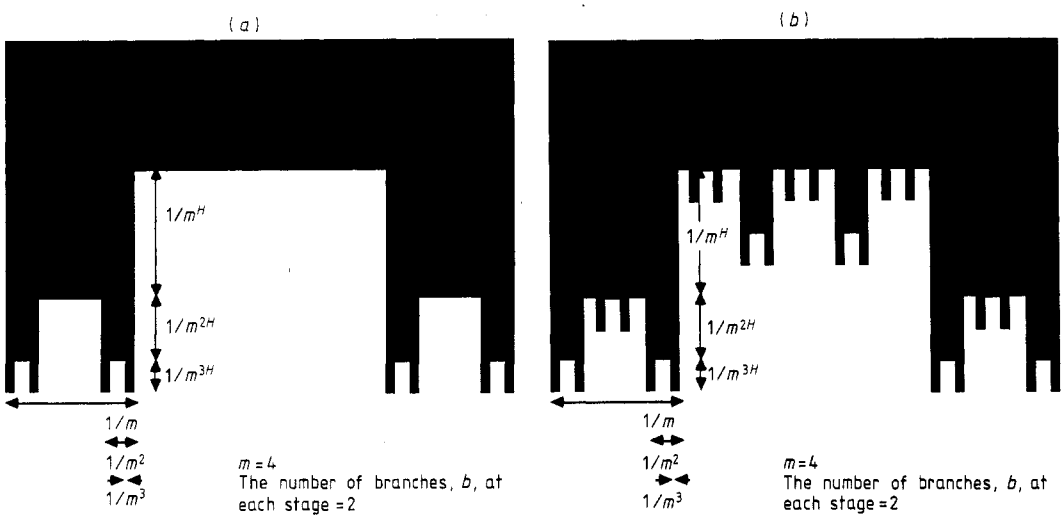

Figure 1. (a) A self-affine model for a rough surface. The electrolyte lies in the black region. (b) A self-affine model with dense structure.

This assumes that $H < \ln(b)/\ln(m)$. For larger H, the largest grooves make the dominant contribution to the arc length and we find, simply, that $d_H = 1$.

To find $S(\Delta)$ we note that at the jth iteration we have b^j jumps of size m^{-Hj}. This gives us, for the smallest grooves dominating the average,

$$d_\Delta = 1 + 2H - \ln(b)/\ln(m). \tag{7}$$

This requires that $\ln(b)/\ln(m) > 2H$. Outside this region we find $d_\Delta = 1$ as $S(\Delta)$ is dominated by the discontinuity in h at the edge of the largest groove. However (7) is recovered if we allow each groove to have sloping sides. We shall introduce the model that the top of each groove is wider than the base by a small but finite fraction.

Notice that the laws, equations (6) and (7), are not consistent with equations (3) and (5), respectively. The scaling analysis assumed we had a surface where the structure was everywhere dense. Figure 1(b) shows a boundary where this is the case. At a stage j we now have bm^{j-1} grooves distributed everywhere along the surface—if the total number of iterations, n, is very large, there are only tiny regions of flat interface. For this model, if we introduce the refinement of slightly sloping sides, to remove the discontinuities in $h(x)$, then we find values of d_H and d_Δ consistent with (3) and (5), respectively.

Liu [11] studied the structure in figure 1(a) where $H = 0$. In his paper the dimension of the surface was given by (6) with $H = 0$.

3. An equivalent circuit analysis

The models proposed above are a crude model of a surface which has been scratched to reveal pits and grooves of many sizes. We are able to calculate the surface impedance, Z, using an equivalent circuit representation. We assume that the interface between the electrolyte and the electrode has a purely capacitive impedance. The electrode is at zero potential. Figures 2(a) and 2(b) show the equivalent circuits for the models illustrated in figures 1(a) and 1(b) respectively. It is then possible to write down the impedance of the surface as a continued fraction. At the zeroth stage the total impedance of the sides of the groove is taken to be $1/i\omega C$ and the electrolyte contained

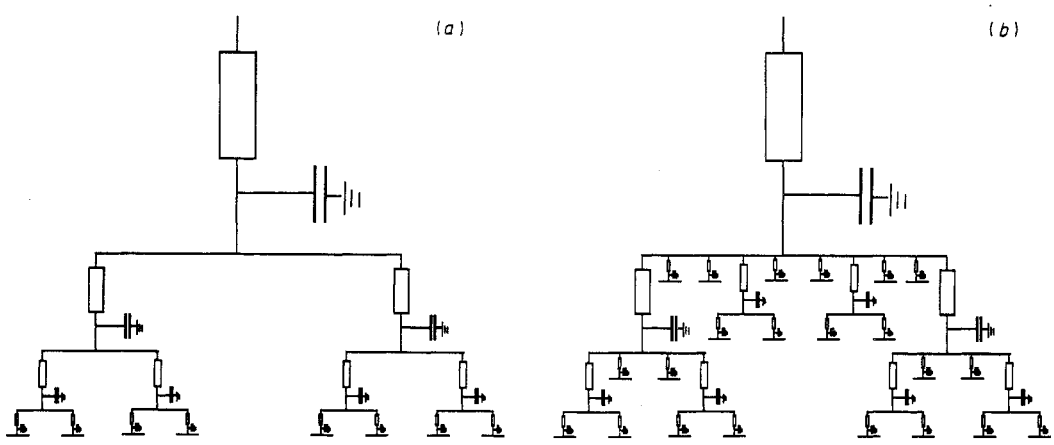

Figure 2. (a) An equivalent circuit for the impedance of the surface shown in figure 1(a). (b) An equivalent circuit for the structure shown in figure 1(b).

within the groove has a resistance Z_e. At the jth stage the groove is m^{Hj} times shorter and m^j times narrower than the original. Hence the capacitance of the sides will be Cm^{-Hj} and the electrolyte resistance will be $Z_e m^{j(1-H)}$. Because the grooves after several stages are very narrow, the contribution to the capacitance at each stage from the exposed ends is ignored. For figure 2(a) we find, using the usual rules for the addition of impedances in series and in parallel,

$$Z = Z_e + \cfrac{1}{i\omega C + \cfrac{b}{m^{1-H}Z_e + \cfrac{1}{i\omega Cm^{-H} + \cfrac{b}{m^{2(1-H)}Z_e + \cfrac{1}{i\omega Cm^{-2H} +}}}}} \tag{8}$$

and for figure 2(b)

$$Z = Z_e + \cfrac{1}{i\omega C + \cfrac{b}{m^{1-H}Z_e + \cfrac{1}{i\omega Cm^{-H} + \cfrac{b}{m^{2(1-H)}Z_e + \cfrac{1}{i\omega Cm^{-2H} +}}}} + \cfrac{(b-1)(m-b)}{m^{2(1-H)}Z_e + \cfrac{1}{i\omega Cm^{-2H} +}} +} \tag{9}$$

where the continued fractions have been written up to the third stage of iteration.

The appendix contains a justification of the equivalent circuit analysis and a discussion of the circumstances in which it is valid.

4. Calculations

Kaplan and Gray [12] used an elegant analysis to show that CPA behaviour could be observed from the impedance Z written out in equation (8), in the case $H = 0$. Here we shall extend the method for any H and for both the fractions given in equations (8) and (9). If we write

$$Z(\omega) = Z_e + \frac{1}{i\omega C + Z'(\omega)} \tag{10}$$

then it is easy to see that if we set $\omega' = \omega m^{1-2H}$ then, if the fraction in (8) is continued for an infinite number of stages,

$$Z'(\omega) = bm^{H-1}/Z(\omega'). \tag{11}$$

This enables us to derive the exact relation:

$$Z(\omega m^{2H-1}) = Z_e + \frac{1}{i\omega m^{2H-1}C + bm^{H-1}/Z(\omega)}. \tag{12}$$

We shall now attempt to find solutions for Z consistent with $Z(\omega) \sim (i\omega)^{-p}$ with $0 \leq p \leq 1$, in the limit of small ω. Then $|1/Z(\omega)| \gg \omega C$ and $|Z(\omega)| \gg Z_e$ and so approximately

$$Z(\omega m^{2H-1}) = Z(\omega) m^{1-H}/b. \tag{13}$$

This has a solution if

$$m^{p(1-2H)} = m^{1-H}/b. \tag{14}$$

We find

$$p = \frac{1-H-\ln(b)/\ln(m)}{1-2H}. \tag{15}$$

This gives p between 0 and 1 for $H \leq 0.5$ where $1-H \geq \ln(b)/\ln(m) \geq H$. Outside this range we can only have consistent solutions for $p = 0$ or 1. This equation was derived by Liu for the case $H = 0$.

Equation (15) immediately enables us to support the conclusion of the experimental work of Bates *et al* [6]: the exponent p and the scaling properties of the surface are not simply related. This is easily demonstrated for the model shown in figure 1(*a*) with $b = 2$ and $m = 4$. In this case $p = 0.5$, independent of H. The impedance behaviour for surfaces with a finite number of iterations, calculated numerically from equation (8), is shown in figures 3(*a*) and 3(*b*) for the cases $H = 0$ and $H = 0.3$, respectively. We have plotted $\log[-\omega\ \mathrm{Im}(Z)]$ against $\log(\omega)$; then, capacitive behaviour is represented by a horizontal line on the graph and CPA behaviour is shown by a straight line

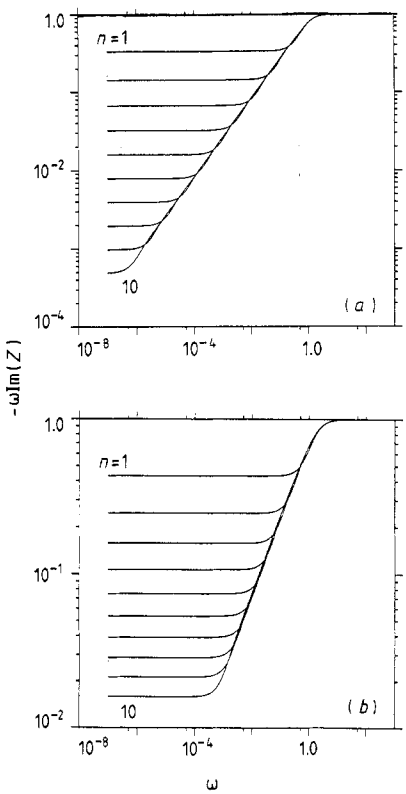

Figure 3. $-\omega\ \mathrm{Im}(Z)$ is plotted against ω on a logarithmic scale, where ω is the frequency and Z is the complex impedance of the surface illustrated in figure 1(*a*) with various stages of iteration, $n = 1$-10, as indicated on the graphs. In these graphs and figures 4-7, ω and Z are measured in units of $1/(Z_e C)$ and Z_e, respectively. CPA behaviour is indicated by a straight line of slope $1-p$. (*a*) $H = 0$. We find that $p = 0.5$. (*b*) $H = 0.3$. Again $p = 0.5$. The values of p are consistent with equation (15).

of slope $1-p$. An impedance behaviour independent of frequency is indicated by a slope of 1. Notice that the impedance is extremely sensitive to surface roughness—even a few hierarchies of grooves generates a power-law over a wide spectrum of frequency.

However, it is also apparent that our analysis breaks down when H exceeds 0.5 or the value of p computed from (15) lies outside the range from 0-1. In such a case we cannot observe an exact CPA law as we increase the number of iterations to infinity. If $\ln(b)/\ln(m)$ is greater than 0.5, then as we increase H from zero, p decreases to zero when $H = 1-\ln(b)/\ln(m)$. In this case we have many branches on the structure. Increasing H allows more hierarchies of branching to be probed by the same length of path through the electrolyte. Thus the surface appears to have an extremely large area. For a capacitive interface the impedance varies as the inverse of the surface area, and so the bare boundary makes an very small contribution to the overall impedance—it is now governed by the electrolyte resistance and is almost independent of the frequency. This is illustrated for the case $b=2$ and $m=3$. In figure 4(a) we have $H=0.3$ and we find $p=0.173$; in figure 4(b) H is 0.4. Here when the impedance departs from capacitive behaviour, we no longer see an exact power law: the graph has an approximate slope equal to 1, which indicates that the impedance is nearly independent of frequency.

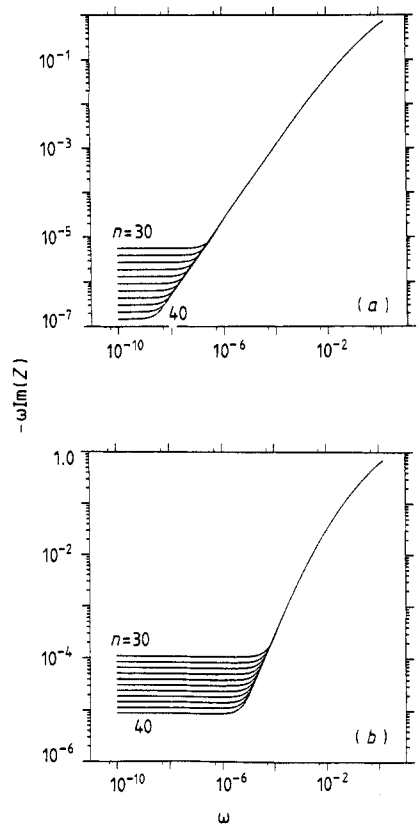

Figure 4. $-\omega$ Im(Z) is plotted against ω on a logarithmic scale for a surface similar to that illustrated in figure 1(a), but with $b=2$ and $m=3$, and for various stages of iteration, $n=30$-40, as indicated on the graphs. (a) $H=0.3$. We find CPA behaviour with p approximately equal to 0.17. (b) $H=0.4$. We no longer see an exact power-law behaviour.

When $\ln(b)/\ln(m)$ is less than 0.5, the branches are sparse and, as we increase H, p increases to reach 1 (normal capacitive behaviour) when $H = \ln(b)/\ln(m)$. In this case, the number of smaller sub-branches is insufficient to make a significant contribution to the impedance. For a surface with a large number of iterations, this is equivalent to truncating the continued fraction after a fixed, finite number of stages. Thus surfaces generated with different numbers of iterations have approximately the same capacitive impedance at low frequency. This is illustrated in figure 5 where $b = 2$ and $m = 6$. In figure 5(a), $H = 0.3$ and we see CPA behaviour with p equal to 0.783. When $H = 0.4$ (figure 5(b)) we can see that we no longer have a power-law impedance, and that $Z \sim 1/i\omega C$ for small ω, even within the range where a CPA law was seen for $H = 0.3$. Viewing the full range of ω in figures 4 and 5 is perhaps of mathematical interest only, since no real surface is likely to contain structure over the range of lengths pertinent for 30 stages of grooves, but the figures do demonstrate the destruction of the CPA law for non-zero H.

The case $\ln(b)/\ln(m) = 0.5$ is critical, with an approximate power-law impedance with $p = 0.5$ seen over a very restricted range of lengths for H greater than 0.5, as shown in figure 6, where $m = 4$, $b = 2$ and $H = 0.7$.

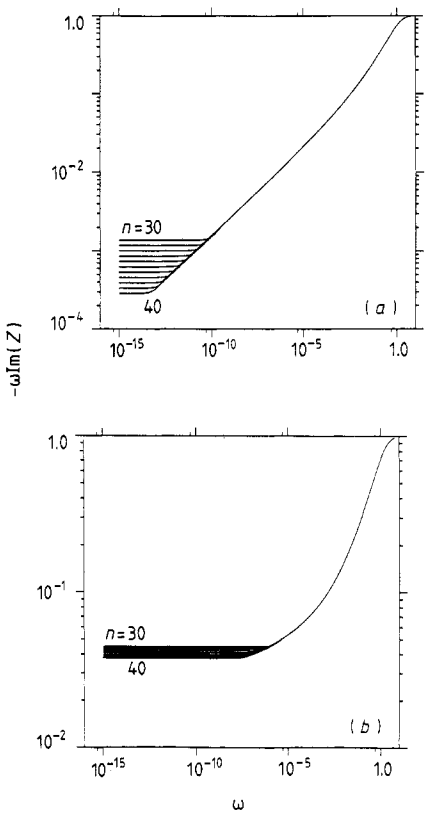

Figure 5. $-\omega\,\mathrm{Im}(Z)$ is plotted against ω on a logarithmic scale for a surface similar to that illustrated in figure 1(a) but with $b = 2$ and $m = 6$, for various stages of iteration, $n = 30$–40, as indicated on the graphs. (a) $H = 0.3$. We find CPA behaviour with p approximately 0.78. (b) $H = 0.4$. We no longer see an anomalous power-law behaviour—for most of the frequency range a simple capacitive impedance is observed.

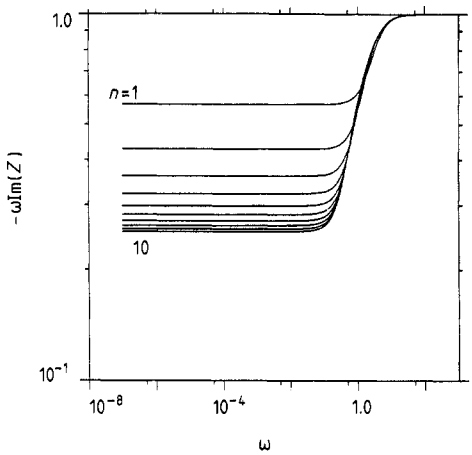

Figure 6. The graph is similar to figures 3-5 above, but here $m=4$, $b=2$ and $H=0.7$. Notice that only an approximate power-law impedance is observed over a restricted range of frequency.

Thus for surfaces with fairly sparse structure we see CPA behaviour—if it is too sparse, the impedance approximately resembles that for a smooth interface and if it is too dense the large surface area gives us an impedance independent of frequency. In these two regimes an approximate power-law behaviour with p between 0 and 1 may be seen, as in figure 6, over a very restricted range of frequency—usually covering only about a decade of frequency, unless we have carefully chosen parameters, which would not explain the many experiments where a CPA law over 5 decades of ω was observed.

5. Impedance for models with dense structure

From the discussion above we now expect that the model with structure which is everywhere dense will not give us a CPA law. The interface will present a very large area to the electrolyte and so we shall have an overall impedance which is very small. We can repeat an analysis identical to that previously for the continued fraction in (9). After some algebra, the effects of the parameters m and b disappear (as they did in the calculation of d_H and d_Δ). Then we find possible solutions for $Z(\omega)\sim(\mathrm{i}\omega)^{-p}$ if

$$p=(1-H)/(1-2H) \tag{16}$$

or

$$p=-H/(1-2H). \tag{17}$$

There are no consistent solutions for $0<p<1$ if $0\leqslant H\leqslant 1$.

In fact, in all cases the total impedance only makes a small correction to the resistance of the original groove. The impedance of the electrolyte is now larger than that of the rough surface it surrounds. Figure 7 shows $\log[|Z(\omega)|-Z_e]$ plotted against $\log(\omega)$, where Z_e is the resistance of the zeroth groove and $Z(\omega)$ is calculated numerically from (9). It can be seen that, after several stages of iteration, the impedance makes just a small correction to Z_e, which is independent of frequency, except for exceptionally small ω where we recover normal capacitive behaviour.

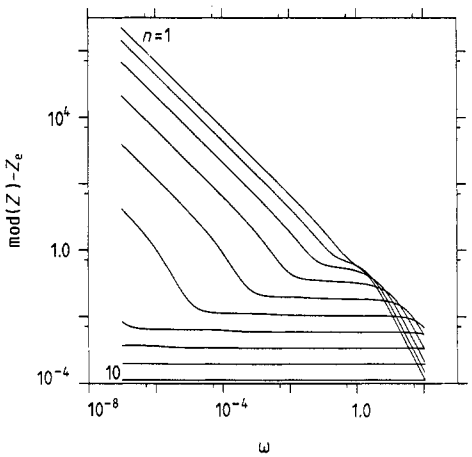

Figure 7. The impedance of a self-affine surface with dense structure. The difference between the modulus of Z, and Z_e, the resistance of the electrolyte at the zeroth iteration (which is taken to be unity), is plotted against frequency, ω, on a doubly logarithmic scale. Equation (9) is used to calculate the impedance of the structure shown in figure 1(b), with $H = 0.5$ and with various stages of branching, $n = 1$–10, as indicated on the graph. Notice that, for models with many stages of branching, the total impedance is independent of frequency and makes a small correction to Z_e, except at extremely small ω.

However, in the experiments of Bates *et al* [6], and most probably much of the work on solid electrolytes, the surface impedance was large compared with that for the electrolyte contained within the surface irregularities. If this is not the case a renormalisation scheme to calculate the impedance may be more appropriate than the analysis given here [19].

6. Fully three-dimensional models

We can also model a fully two-dimensional surface, where each groove, instead of being extended indefinitely in a plane perpendicular to the cross sections illustrated, has a length equal to its width (m^{-j} at the jth stage of iteration). b again represents the number of new grooves, or holes, generated at each stage. For a dense structure we now must have of order m^{2j} branches at stage j. A repeat of the analysis above yields similar results: we do not see a CPA law for dense branching, but for a surface similar to that shown in figure 1(a), we obtain, instead of equation (15),

$$p = \frac{2 - H - \ln(b)/\ln(m)}{1 - 2H} \tag{18}$$

with solutions for $H < 0.5$ and $2 - H \geqslant \ln(b)/\ln(m) \geqslant H$.

7. Conclusions

We can now present a clear physical picture of the impedance of self-affine surfaces. We observe CPA behaviour for surfaces whose structure is sparse. That is, most of the surface is smooth when viewed at a fine resolution, with the grooves distributed along

the interface. We calculate the impedance by considering the various current paths to the electrode. At each stage of branching, there are routes to the electrode across smooth capacitive portions of surface as well as routes through the electrolyte to smaller sub-branches. The total impedance is very sensitive to surface roughness, with a power-law behaviour observed over a wide range of frequencies for only a small number of stages of structure. The exponent p is not simply related to the scaling of the geometry of the interface, H. Depending on the structure, p may increase, decrease or remain constant on the variation of H with all other parameters remaining constant. p is dependent on both H and the degree of sparseness of the structure, which is measured by the ratio $\ln(b)/\ln(m)$. If the features are dense along the boundary, then the very large number of branches causes a considerable reduction in the impedance from an interface with fewer grooves. For interfaces sufficiently dense with grooves, which includes all boundaries which are everywhere rough except on the scale of the finest features, the surface impedance becomes independent of frequency and makes only a small correction to the overall resistance of the electrolyte contained by the surface irregularities. Then we no longer see CPA behaviour.

The calculation of a CPA law in this paper is applicable to an electrode with sparse small-scale unevenness surrounded by a medium with a large conductivity. This is likely to be the case for electrodes which are made rough by scratching grooves on the surface. Moreover, Kaplan and Gray [12] demonstrated that a random surface, with the branching ratio, b, and the change in scale, m, different at each iteration, still gave a power-law behaviour, although they only studied the case $H = 0$. Further work on these surfaces demands a more detailed independent characterisation of the geometry. In particular, for boundaries whose structure is not everywhere dense, the exponents H, d_Δ and d_H are unlikely to be simply related. The experiment of Bates *et al* [6] only inferred d_Δ from an analysis of the surface geometry over a small range of size. It is not clear that the results would be unaltered if a more sensitive probe were used to investigate the surface, or indeed, especially for boundaries with a sparse structure, that d_Δ is a good reliable measure of the interfacial unevenness. One test is to make a contour map of a typical portion of the electrode, perhaps using scanning tunneling electron microscopy, and then calculate the impedance numerically for that surface. This hopefully should agree with an experimental determination and would show that CPA behaviour is governed sensitively by the surface geometry.

Acknowledgments

Helpful discussions with M E Cates and R C Ball are gratefully acknowledged. MJB also thanks British Petroleum and the SERC for financial support.

Appendix. Justification of the equivalent circuit analysis

Although the representation of the impedance as a continued fraction is very appealing and allows Z to be calculated directly, it is necessary to consider under what conditions the analysis is valid. No justification was offered in the Liu paper.

Figure A1 shows an attempt at a solution for ϕ, the potential in a single groove, at the zeroth stage, of width $2X$ and depth Y ($Y > X$), whose sides have a total impedance $1/i\omega C$ with a constant end impedance Z_{end}. On the boundaries of the

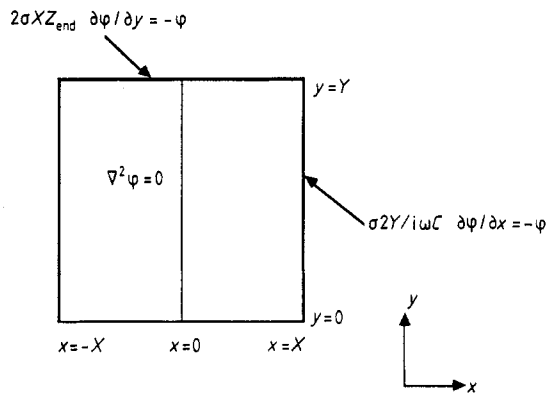

Figure A1. A solution for the electrostatic potential in an inverted groove. The potential obeys Laplace's equation and the boundary conditions indicated.

groove, the normal current density is $\sigma\,\partial\phi/\partial n$. σ is the electrolyte conductivity and $\partial\phi/\partial n$ the electric field normal to the surface. The current density also equals ϕ/z_s, where z_s is the surface impedance for unit area (or unit length in this two-dimensional calculation). This gives us a surface boundary condition:

$$\sigma\,\partial\phi/\partial n = \phi/z_s. \tag{A1}$$

We can find a solution for ϕ in two limits.

(i) $|\omega CZ_e| \ll 1$. This means that the electrolyte impedance in the groove is much smaller than that of the surface. The potential varies slowly within the groove and the electric field penetrates all parts of the structure. We write

$$\phi = \phi_0[1 - c_1 y + c_2(y^2 - x^2) + \ldots] \tag{A2}$$

where $|c_2 Y^2| \ll |c_1 Y| \ll 1$. The coefficients c_1 and c_2 are found by applying boundary conditions of the form of equation (A1) on the boundary of the groove (see figure A1).

Then we define the impedance of the whole structure as

$$\frac{1}{Z} = -\int_{-X}^{X} \mathrm{d}x \frac{\sigma}{\phi} \frac{\partial\phi(x, y)}{\partial y} \tag{A3}$$

where the derivative is evaluated at $y = 0$.

The condition $|c_1 Y| \ll 1$ implies that $|Z_e| \ll |Z_{end}|$ and $|c_2 Y^2| \ll |c_1 Y|$ means $|\omega CZ_e| \ll 1$. We find

$$Z = \frac{Z_{end}}{1 + Z_{end}\,i\omega C}\left(1 + \frac{Z_e}{Z_{end}} - \frac{Z_e}{(2/i\omega C)(1 + i\omega CZ_{end})}\right) \tag{A4}$$

where $Z_e = Y/2\sigma X$ and is the resistance of the electrolyte within the groove. If the equivalent circuit were valid we would find

$$Z = \frac{Z_{end}}{1 + i\omega CZ_{end}}\left(1 + \frac{Z_e}{Z_{end}} + i\omega CZ_e\right). \tag{A5}$$

The two expressions are only equivalent if $|\omega CZ_e|$ is much less than 1.

The analysis is still valid for a groove with slightly sloping sides, with Z_e and C again representing the total electrolyte resistance and surface capacitance respectively.

We have still not solved for an impedance at the bottom of the groove which varies with position—if the change in scale at each iteration is large, then we still believe the analysis to be accurate, with Z_{end} representing the total impedance of the sub-branches added in parallel, with the variation in impedance for unit length only affecting ϕ on scales much smaller than the overall size of the groove.

(ii) $|\omega C Z_e| \gg 1$. In this case the electrolyte resistance dominates and the electric field fails to penetrate the structure.

We write a solution:

$$\phi = \phi_0 \exp(-cy) \cos(cx) \tag{A6}$$

where $|cY| \gg 1$.

The boundary condition on the sides of the groove reveals that

$$c \tan(cX) = i\omega C Z_e X / Y^2 \tag{A7}$$

and if $|cX| \ll 1$ we find

$$c^2 Y^2 = i\omega C Z_e \tag{A8}$$

and the overall impedance Z, from equation (A3) is

$$Z = Z_e / cY \tag{A9}$$

which is smaller than Z_e and independent of Z_{end}, i.e. the smaller grooves arranged at the base. The equivalent circuit analysis is no longer valid.

In this analysis the conditions $|cX| \ll 1$ and $|cY| \gg 1$ mean that $Y^2/X^2 \gg |\omega C Z_e|$. This condition is also satisfied for thin grooves when $|\omega C Z_e|$ is small.

As we consider further stages of iteration the grooves become relatively thinner, increasing the overall resistance of the electrolyte contained in the grooves. For the jth stage of iteration the equivalent circuit representation will only be valid for $|\omega C Z_e m^{j(1-2H)}| \ll 1$. We assume that at the zeroth stage $|\omega C Z_e|$ is small. Then there are two cases to be considered.

(i) $H > \frac{1}{2}$. The condition $|\omega C Z_e m^{j(1-2H)}| \ll 1$ always holds and the equivalent circuit analysis is valid to all orders of iteration. The electric field penetrates all sections of the structure. This means that the field probes an extremely large surface and leads to an overall impedance that is very small. We shall show that, in this case, we do not see CPA behaviour.

(ii) $H < \frac{1}{2}$. It is clear that, as we increase j, the condition $|\omega C Z_e m^{j(1-2H)}| \ll 1$ will no longer hold: at small scales the electrolyte resistance is larger than the surface impedance. The electric field will eventually become unable to penetrate the small thin surface irregularities. As we vary the frequency different hierarchies of structure are probed. For a fractal surface we shall show that this can lead to a power-law relation between the impedance and ω and we do see CPA behaviour in some cases.

Therefore, when we consider the impedance of a surface with many stages of branching and $H < \frac{1}{2}$ the equivalent circuit analysis is valid for j iterations until $|\omega C Z_e m^{j(1-2H)}| > 1$. The flux does not penetrate the smaller grooves and so the fractions (8) and (9) are effectively terminated at this jth stage. This relates a spatial length scale on the surface with a frequency cutoff for CPA behaviour. However, an examination of equations (8) and (9) reveals that when $|\omega C Z_e m^{j(1-2H)}| \gg 1$ the contribution to the fraction from larger j is negligible. Thus the fraction naturally terminates, albeit in a different manner, at the stage when the equivalent circuit representation is no longer applicable. This indicates that (8) and (9) do give an adequate representation

of the surface impedance for all frequencies, ω, if $Y^2/X^2 \gg |\omega C Z_e m^{j(1-2H)}|$. However, a note of caution is needed here. The analysis can only investigate the impedance of a surface composed of tall thin grooves. The experiments of Bates *et al* [6], in contrast, indicated that on the largest scales the electrolyte surface consisted of only gently undulating structure. It is clear that eventually any self-affine surface would appear steep at a sufficiently fine resolution but, unfortunately, this could not be resolved by the probe used.

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