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1988 J. Phys. A: Math. Gen. 21 197

(http://iopscience.iop.org/0305-4470/21/1/024)

J. Phys. A: Math. Gen. **21** (1988) 197–204. Printed in the UK

A fractal model for the impedance of a rough surface

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Received 13 March 1987, in final form 24 August 1987

Abstract. We present a fractal model for a rough interface between an electrode and an electrolyte. We calculate that the complex surface impedance is $Z = K(Z_0)^p$ where Z_0 is the impedance of a flat interface. If the fractal dimension, d_f, of the boundary is written as $2+\delta$, where δ is small, then, to first order in δ, $p = 1-2\delta$. For a purely capacitive interface, $Z_0 = 1/i\omega C$; this gives an anomalous power-law frequency dependence as seen experimentally by Bottelberghs and Broers and by Armstrong and Burnham. We explicitly calculate the prefactor K and the range of frequency for which this law is observed in terms of the range of lengths over which the interface is rough.

1. Introduction

We shall first consider a flat metal electrode in contact with an electrolyte. Free ions in the electrolyte can produce a current and oxidation and reduction of the species, as well as the electronic current, allows some charge to be transferred across the surface. If a voltage is applied, a net charge builds up near the interface to screen the potential. The width of this polarised region is given by the Debye length [1], λ_D, $\lambda_D^{-2} = ne^2/kT\varepsilon_0$, where n is the ionic concentration. Typically the Debye length is several ångströms (see, for instance, [2])†. Outside this layer, the current in the electrolyte can be modelled by the equivalent circuit of a surface impedance, Z_s, in series with a bulk electrolyte impedance, Z_e. If the charge transfer current is small, then Z_s is a capacitance, while Z_e is a resistance. The capacitance per unit area is ε_0/λ_D and so can be very large. However, for Z_s to behave like a linear circuit element, we require the potential across the boundary to be less than kT/q, where q is the ionic charge. In our analysis we shall assume that the current density is small, that outside the Debye layer the ionic concentration is constant and that the surface layer does behave like a linear circuit element, independent of the direction of the potential difference. This means that we have ignored corrections from the detailed chemistry of the interface, the convection of the ions and the electrical anisotropy of some single crystal solid electrolytes. We can then write the impedance of the system as

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

However, de Levie [4], Bottelburghs and Broers [5], Armstrong and Burnham [6], and Bates *et al* [7] discovered an anomalous frequency dependence if the contact

† For example, the Debye length of β alumina, discussed later in this paper, is less than an atomic diameter [3].

0305-4470/88/010197+08$02.50

between the electrode and a solid electrolyte† was rough. They obtained an impedance:

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

where $0 < p \leq 1$.

This constant phase angle dependence was found to hold in many systems for up to five decades of frequency, with p varying from 0.39 to 0.98. Armstrong and Burnham [6] 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 as the electrode became rougher. When it was polished, p approached 1. Since a power-law impedance is observed, it was reasonable to suggest that this could be derived from a self-similar boundary with p related to the fractal dimension. This was done by Liu [11] and extended by Kaplan and Gray [12], who described the contact as an arrangement of parallel grooves. Halsey [13] has also recently looked at the problem and it was his study that prompted the present work. He considered the interface as a supposition of mountains and valleys of different sizes.

We use a fractal model of the interface from which the law (2) emerges naturally as part of a renormalisation flow diagram. The method used could be applied to a variety of other problems with a fractal boundary condition‡. We uncover a richer behaviour than that found previously.

2. Calculations

Consider now a crinkled boundary between the electrolyte and the electrode, where the size of the crinkles is greater than the screening length. See figure 1. In the electrolyte, beyond the polarised layer of charge, $\nabla^2\phi = 0$, where ϕ is the electrostatic potential. On the boundary of this layer, the normal current density is $j_n = \sigma\partial\phi/\partial n$, where σ is the electrolyte conductivity and $\partial\phi/\partial n$ is the electric field normal to the surface. j_n is also equal to ϕ/z_s, where z_s is the surface impedance for unit area. This gives us the surface boundary condition

$$\sigma\partial\phi/\partial n = \phi/z_s. \tag{3}$$

First we shall do the calculation in two dimensions. Then z_s is the impedance for unit length and σ has the dimensions of (resistance)$^{-1}$. For a flat electrode of width L_x, the total impedance for an electrolyte of length L_y is simply $L_y/(L_x\sigma) + Z_s$ with $Z_s = z_s/L_x$. Remember that we have added the impedance z_s in parallel across the interface to find Z_s.

We now slightly buckle the electrode such that the double layer of charge lies along the curve $y = a\cos(kx)$, where $ak = \varepsilon \ll 1$, but $a > \lambda_D$. We call the wavelength of this perturbation λ_{min}. We now solve Laplace's equation in the electrolyte with the boundary condition (3) on the curve and where the electric field, $\partial\phi/\partial y$, is constant for large y. We further assume that $Z_s \ll Z_e$, i.e. most of the impedance is carried by the electrolyte. We can find an analytic solution for ϕ as a power series in ε, the dimensionless amplitude of the buckling. The plate now has a slightly longer length and so we should

† A description of the theory and applications of solid electrolytes is given in [8, 9] while [10] is particularly useful.

‡ The authors have used the same fractal model to describe the velocity distribution at the fluid boundary in viscous fingering [14].

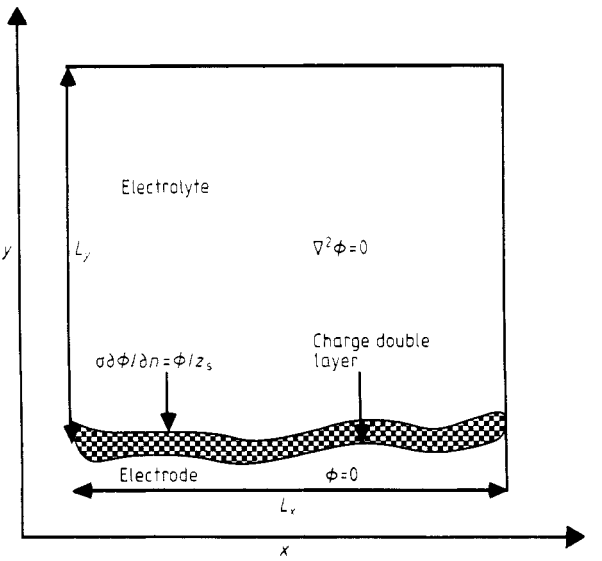

Figure 1. Diagram explaining the equations and boundary conditions used to calculate the interfacial impedance of an electrode in contact with an electrolyte. The layer of charge is much thinner compared with L_x than shown in the diagram. There is another identical interface at the other electrode.

expect to find an increase in the capacitance as well as a small alteration of the overall resistance, because of the variation in height. Working to $O(\varepsilon^2)$ we obtain

$$Z_s^1 = Z_s - \frac{\varepsilon^2 L_x}{4\sigma k}\left(\frac{R^2+R+2}{R+1}\right). \tag{4}$$

Z_s is the surface impedance of the flat plate and $R = k\sigma z_s$. R is a dimensionless comparison of the surface and electrolyte impedances.

We model a fractal interface by considering a sequence of bucklings [14]. Imagine that the plate is further crinkled by another wave of arbitrary phase with respect to the first, with a larger wavelength, $m\lambda_{min}(m>1)$, but the same dimensionless amplitude ε (figure 2). This is not the simple addition of two waves; the original sinusoidal perturbation is perpendicular to the second. We continue this process for a large number, N, of bucklings until we reach $\lambda_{max} = m^N\lambda_{min}$. Here λ_{max} represents the size of the largest roughenings on the boundary. The boundary is self-similar. This process may be regarded as a smooth but statistical adaptation of the Koch curve construction [15]. Two fully developed curves are shown in figure 3. We measure the fractal dimension d_f by considering the increase in apparent arc length at each change of scale [15]:

$$d_f = 1 + \varepsilon^2/4 \log m - 3\varepsilon^4/64 \log m + O(\varepsilon^6). \tag{5}$$

We now calculate the interfacial impedance of this structure. That is, what is the surface impedance of the fractal boundary if the impedance per unit length is z_s?

For the first buckling, the electric field is roughly constant beyond a distance $1/k$ from the interface. Consequently, on scales much larger than this we can consider the system to be equivalent to a flat plate with an effective impedance per unit length, z_s^1, such that $z_s^1/L_x = Z_s^1$ in (4). If $m \gg 1$, the second buckling will be much larger than

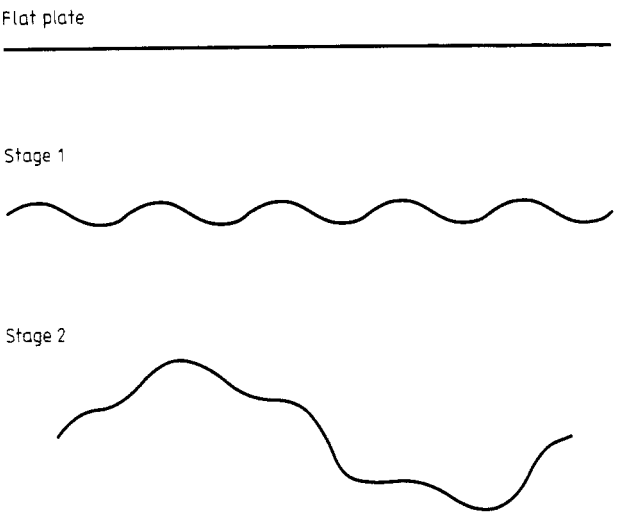

Figure 2. The first two stages in the generation of the model fractal. We would calculate the impedance of stage 2, for instance, by considering the smaller scale crinkles smoothed out, but with a modified impedance per unit length obtained from equation (6). Repeating this many times would give the impedance of a multiply-buckled interface.

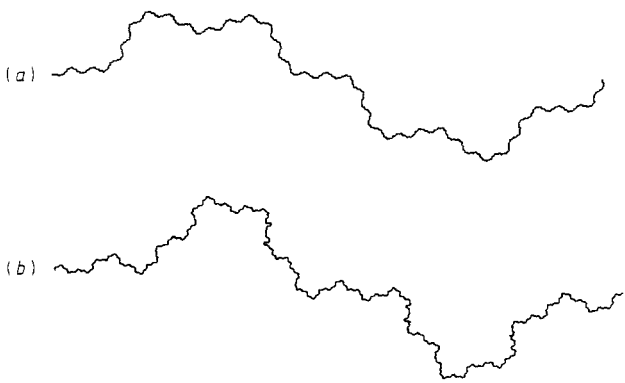

Figure 3. The interface after many stages of buckling. (*a*) $m=5$, $\varepsilon=0.8$ and $d_f \approx 1.09$. (*b*) $m=3$, $\varepsilon=0.8$, $d_f \approx 1.13$. The large value of ε is chosen so that the discrete stages of buckling can be clearly seen. See also [14].

the first. We can consequently find the impedance of the doubly crinkled interface from (4), but with z_s replaced with the z_s^1 calculated from the first stage. Repeating this procedure enables us to calculate the impedance for the fully crinkled system. We obtain a recursion relation. For the nth buckling of wavenumber $k_n = m^{-n}k$:

$$Z_s^n = Z_s^{n-1} - \frac{\varepsilon^2 L_x}{4\sigma k_n}\left(\frac{R^2+R+2}{R+1}\right) \tag{6}$$

where now $R = k_n \sigma z_s^{n-1}$ and $Z_s^n = z_s^n / L_x$.

Any self-similar structure can be thought to be built up from the same pattern repeated on many scales. However, a complete description of any given boundary would be extremely difficult. We have only been able to solve the problem for small

perturbations well separated in length. Each buckling makes a small fractional change to the surface impedance, but the total change after many bucklings can be very large. Despite the simplicity of the model, the calculation reveals a rich behaviour. Equation (6) not only alters the modulus, but also the argument of Z_s^n. Consequently z_s may be imaginary, but the final impedance need not be so.

Equation (6) gives the small change in Z_s^n each time n increases by 1. We write $x = \log(\lambda_n/\lambda_{\min})$ and consider this a continuous function. Hence we can write

$$\frac{\partial Z_s^n}{\partial x} = -\frac{\delta L_x}{\sigma k_n}\left(\frac{R^2+R+2}{R+1}\right) \tag{7}$$

where we have written $\varepsilon^2/4\log m$ as δ and $\delta < 1$.

This can be arranged to give a differential equation for R

$$\frac{\partial R}{\partial x} = -\delta\left(\frac{R^2+R+2}{R+1}\right) - R. \tag{8}$$

This is easily integrated using the initial condition that, when $x = 0$, $R = R_0 = 2\pi\sigma z_s/\lambda_{\min}$. We obtain

$$(1+\delta)(r_+ - r_-)x = -(1+r_+)\log\left(\frac{R-r_+}{R_0-r_+}\right) + (1+r_-)\log\left(\frac{R-r_-}{R_0-r_-}\right) \tag{9}$$

where $r_+ = -2\delta + O(\delta^2)$ and $r_- = -1+2\delta+O(\delta^2)$.

A flow diagram showing the behaviour of R for different values of R_0 is shown in figure 4. As we include more and more bucklings, the flow tends towards a fixed point at r_+ which is negative and real; hence the fully crinkled interface makes a small negative correction, $Z^* = -\delta\lambda_{\max}/\pi\sigma L_x$, to the overall resistance of the electrolyte. The quantity $R - r_+$ is of some interest. If $|R_0| \gg 1$, which will almost always be the case for small $\lambda_{\min}$ and low frequency impedance measurements, we have

$$R - r_+ = (R_0)^{1-2\delta}(\lambda_{\max}/\lambda_{\min})^{-(1-\delta)}. \tag{10}$$

Thus the interfacial impedance is

$$Z_s^N = Z^* + K(Z_s)^p \tag{11}$$

where $K = [\lambda_{\min}\lambda_{\max}/(2\pi\sigma L_x)^2]^\delta$ and $p = 1-2\delta+O(\delta^2)$.

Remember also that $d_f = 1+\delta+O(\delta^2)$ from (5). If $Z_s = 1/i\omega C_0$, we obtain (2). Notice though that our analysis gives the impedance for any combination of circuit elements. In particular, R_0 could contain a contribution from an electronic charge transfer resistance or a reactive component to the electrolyte conductivity. The total impedance of the system still includes Z_e, from the electrolyte. Usually Z_e is a resistance and so does not affect the overall frequency dependence. The conductivity of the medium, σ, only alters the prefactor K. If the surface impedance for a flat electrode is negligible (i.e. Z_s is very small), then the anomalous power-law behaviour may not be detectible. The only change in the impedance for the fractal boundary will then be from Z^*, which is real.

The model is easily extended to three dimensions by using bucklings of the form $y = a\cos(\boldsymbol{k}\cdot\boldsymbol{r})$. If all the $\boldsymbol{k}_n$ are parallel, this models a set of parallel undulations, but a criss-crossing system is generated if each $\boldsymbol{k}$ has a random orientation. We arrive at the same value of p, but now $d_f = 2+\delta$. This is different from the work of Liu [11], who found $p = 1-(d_f - d + 1)$, where d is the space dimension. To order δ, we have $p = 1-2(d_f-d+1)$. However, it must be emphasised that p need not be a function of d_f only. For a real self-similar boundary, the fractal dimension is a statistical property

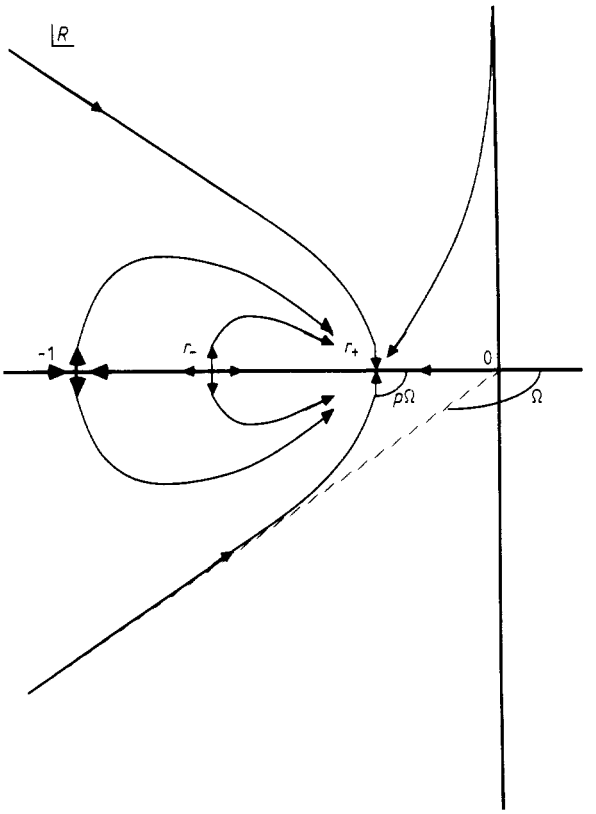

Figure 4. Flow diagram showing the behaviour of R, which is proportional to the interfacial impedance. The diagram is symmetrical about the real axis. The bold arrows indicate the singularity in $\partial R/\partial x$ at -1. The small arrows indicate how the flow moves towards the fixed point at r_+ as we consider more bucklings. If the interfacial impedance per unit length is a pure capacitance and the electrolyte conductivity is real, we follow the flow starting on the imaginary axis. Other combinations of circuit elements start at other points on a circle of large $|R|$. If the flow line makes an angle Ω to the real axis at large $|R|$, then it approaches r_+ at an angle $p\Omega$.

dependent on its geometry. Other exponents, such as p, which involve the surface as a boundary condition in a physical system, will be derived from other statistical properties of the coordinates that describe the surface. Not only does this mean, in this instance, that p is not the same as d_f, but that, in general, no exact relation can be found between them. We illustrate this here by repeating the two-dimensional calculation to $O(\delta^2)$. After a lot of algebra, we obtain $p = 1 - 2\delta - \frac{3}{4}\delta^2 \log m$ with r_+, the fixed point, at $-2\delta + 2\delta^2(\log m - 1)$ and $d_f = 1 + \delta - \frac{3}{4}\delta^2 \log m$. To describe the physics we need two independent parameters, δ and m (or ε and m). Of course, as δ is small, p and d_f are approximately related, but a full theory would involve an infinite set of such parameters and different statistical properties of these would be involved in the description of different scaling relations.

We also performed the analysis for a fully three-dimensional system of crinkles of the form $y = a\cos(kx)\cos(kz + \varphi)$, where the flat plate lies in the xz plane. This produces a square grid of sinusoidal humps. Again $p = 1 - 2\delta + O(\delta^2)$ and $d_f = 2 + \delta$, but $r_+ = -\sqrt{2}\delta$.

The range of frequency for which this power-law or constant phase angle (CPA) regime is observed tells us the range of lengths over which the surface is rough. From now on we shall take R_0 to be imaginary, so we say that the flat polarised layer is a capacitance. The analysis though can still be performed for any set of circuit elements. In the high frequency limit $|R_0|$ is not large, but the flow lines still end up near the fixed point. We find that $Z_s^N = Z' + 1/i\omega C_\infty$. We have normal capacitive behaviour. If C is the capacitance of the flat interface, C_∞ is larger and given by: $C_\infty = C(\lambda_{max}/\lambda_{min})^\delta$ and $Z' = Z^*[1-(\lambda_{min}/\lambda_{max})^\delta]$. The CPA law is valid if $2\pi\sigma L_x/\omega C\lambda_{min} \leqslant 1$.

For extremely low frequencies, the flow never gets near the fixed point and $Z_s^N = 1/i\omega C_0$. Again $C_0 = C(\lambda_{max}/\lambda_{min})^\delta$. Notice that $C_0, C_\infty \gg C$. The CPA law is valid for $\omega C\lambda_{min}/2\pi\sigma L_x \geqslant (\lambda_{min}/\lambda_{max})^{1+\delta}$. This tells us that the range of frequencies obeying the power-law behaviour is:

$$\omega_{max}/\omega_{min} \leqslant (\lambda_{max}/\lambda_{min})^{1+\delta}. \tag{12}$$

3. Conclusions

Bottelberghs and Broers [5] looked at the solid electrolyte Na_2WO_4-Na_2MnO_4 and measured its interfacial impedance in contact with polished Pt and painted Pt electrodes. Armstrong and Burnham [6] did the same with sintered discs and single crystals of β alumina with gold electrodes. They roughened the alumina by polishing with diamond tips of varying size and took electron micrographs of the electrode which coated the electrolyte surface. Bates *et al* [7] also studied β alumina. In all the experiments the electrolyte impedance, Z_e, was larger in magnitude than the surface impedance, Z_s. However, Z_e was a pure resistance and hence Z_s was the only frequency-dependent contribution to the overall impedance. CPA behaviour was found for the polished Pt electrodes and the sintered discs of β alumina. Our analysis would be inapplicable to the single crystal as its conductivity is highly anisotropic, but should give some indication of the geometry of the other samples, particularly where p is close to 1 and hence δ is very small. From the range of frequencies for which the anomalous behaviour is seen, as well as the values of p, we calculate that $\lambda_{max}/\lambda_{min}$ is roughly 1000 for the painted Pt system and between about 10 and 50 for the sintered disc/gold experiment of Armstrong and Burnham. For the former case we have $p = 0.64$ and hence $d_f = 2.18$, while for the latter case we have $p = 0.39$–0.99 and hence $d_f = 2.31$–2.00. We have used $d_f = 2 + \delta$.

From the electron micrographs, the boundary of the gold electrodes is flat above a few μm. Below these scales we see criss-crossing grooves for the single crystals and pits and bumps for the sintered discs. Given the approximations of this model and the complications in the experimental set-up, there is little purpose pursuing the predictions of the theory much further. However, it would be interesting to repeat similar experiments where the surface was known to be fractal and its dimension could be measured independently.

We have presented a simple, yet powerful theory that gives a physical understanding of the anomalous impedance of a fractal surface. It allows us to provide a crude estimate of the degree of surface roughening and its scale in the experiments. Moreover, the method of calculation could be extended to describe other fractal systems.

Acknowledgments

RCB is very grateful for discussions with T C Halsey. MJB acknowledges a CASE studentship from the SERC and British Petroleum plc.

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