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# Effects of microgeometry on the permittivity of impregnated porous media

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**Abstract.** We propose a new approximative relation for the low-frequency dielectric permittivity of liquid-filled porous materials. In this formulation, effects of microgeometry are included through the so-called  $\Lambda$  parameter. Our measurements on salt-water-impregnated artificial sandstones support the new relation. We also show that the high permittivities at low frequencies reported earlier for brine-impregnated sintered glass spheres (Nøst *et al* 1992 *Phys. Scr.* T **44** 67) may be due to effects at the solid–liquid interface in the ‘bulk’ porous material. The latter results are also in agreement with our proposed relation.

## 1. Introduction

The dielectric properties of porous solids, where the pores are filled with a liquid, are of great practical interest. Insulation systems consisting of a porous polymer impregnated with an insulation liquid are a good example, and the need for dielectric characterization is in this case obvious. Dielectric measurements can also be used as a non-destructive diagnostic tool, e.g., for determining humidity in cement [1], or for oil exploration. In the latter case, when porous rock containing water and oil is encountered, electrical measurements are used as a ‘well logging’ tool [2].

Very high values of the relative permittivity at low frequencies have been reported for porous materials filled with salty water [2–6]. This could be dismissed as ‘electrode effects’, but the behaviour could also be due to properties of the ‘bulk’ porous material, for example the solid–liquid interfaces. In certain cases it has been shown [3, 6–9] that the main part of this effect in fact originates within the bulk.

In previous papers [8, 9], we showed that the measured high values of the permittivity at low frequencies for brine-impregnated artificial sandstones could be due to diffusion effects within the electrochemical double layer at the solid–liquid interface. These effects cause the relative permittivity of the layer to exceed by far that of the environment. We used the grain consolidation model [10–12] to calculate the dielectric behaviour of a porous material including a double layer. We compared the results with measured data from artificial sandstones made of glass beads or beach sand together with small amounts of epoxy. The agreement was reasonably good, even though we used a rather crude model for the double layer.

Much of the research in this field concerns the problem of determining the relationship between the properties of the composite material and the properties of its constituents and their relative abundance in the composite. Bergman [13, 14] and Milton [15]

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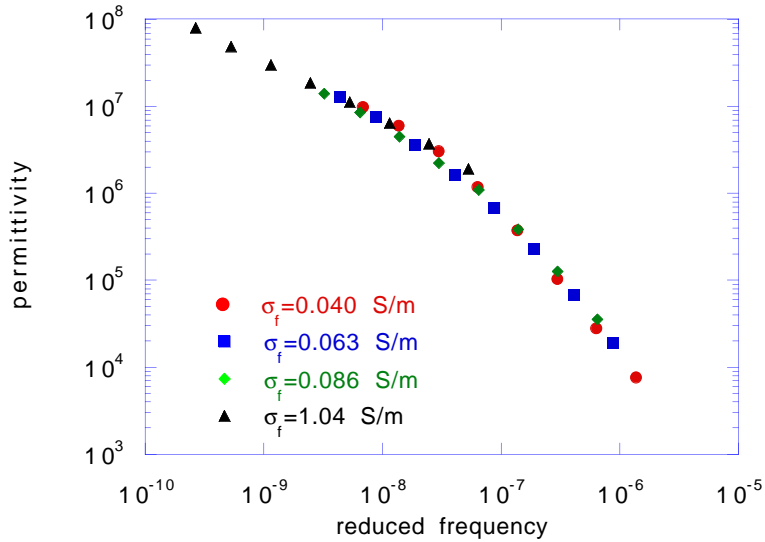
have shown that the properties of a composite material depend on the properties of the constituents and a characteristic geometric function that takes into account the dependence on microgeometry. The characteristic geometric function should thus be the same for various physical properties—for example, for the dielectric constant as well as for the conductivity. It should also be independent of frequency. In this paper we compare the experimental low-frequency permittivity with two models. One is a novel relation for the bulk permittivity, based upon an analogue with established relations for the DC conductivity. The other is a model assuming that electrode polarization is dominating the frequency response. We find that the relation for the bulk permittivity is in better agreement with experimental data.

## 2. Experiments

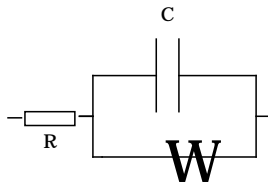
We have performed dielectric measurements and fluid permeability measurements on artificial sandstone samples made of Danish beach sand grains that were glued together with small amounts of epoxy. Before the epoxy was cured, the samples were subjected to pressures in the range 0.2–10 MPa. The samples were prepared to attain a log-normal distribution of grain diameters with a median value of 0.25 mm. The porosity depended on the applied pressure and had values between 0.19 and 0.46. The porosity was measured with a helium porosimeter. The fluid permeability was measured with a variable-head permeameter [16]. Results from such measurements on these samples have been published before [17]. The electrical measurements were taken at frequencies between 5 Hz and 13 MHz with an HP 4192A impedance analyser. The samples were placed in a test cell between brass electrodes. We used a guard electrode to eliminate the influence of conduction on the external surface of the sample. The electrodes were mounted on plastic screws, which enabled us to measure samples with different thicknesses and to achieve a good contact between the sample and the electrodes. The samples were impregnated in a vacuum chamber, that was evacuated to 0.1 Torr before letting the slightly saline water into it (we used water with conductivity values between 0.008 and 1.2 S m<sup>-1</sup>).

To compare measurements taken at different fluid conductivities, we used the so-called reduced frequency [5],  $\omega_w$  ( $\omega_w = \omega \varepsilon_0 \varepsilon'_f / \sigma_f$ , where  $\varepsilon_0$  is the permittivity of vacuum and  $\varepsilon'_f$  and  $\sigma_f$  are the relative permittivity and conductivity of the fluid). The reduced frequency is a dimensionless number, and reflects the common characteristic of the dielectric spectrum of liquid-filled porous solids that it can be scaled in frequency with the conductivity of the pore liquid. In figure 1, the measured permittivity is shown as a function of reduced frequency for a single sample, impregnated with salty water with different conductivities. Measurements with different values of  $\sigma_f$  fall on a well-defined single curve. We observe a frequency dependence of roughly  $\omega^{-0.5}$  at low frequencies, crossing over to  $\omega^{-1.5}$  at higher frequencies.

Åhlén [18] found that the epoxy appeared to be homogeneously and isotropically distributed within the samples, primarily at grain contacts. He estimated that the meniscus of epoxy between the grains decreased the specific surface area by a factor of 0.92. Our earlier results [8] showed that the low-frequency permittivity of these artificial samples resembled the permittivity of natural sandstones with low clay content. We have also performed measurements on dry samples in vacuum; in those measurements, a very low dispersion was found (values of  $\varepsilon'$  at 0.1 Hz between 3 and 7).



**Figure 1.** The apparent permittivity of a salt-water-impregnated artificial sandstone sample as a function of reduced frequency. The measurements have been taken for several liquids differing in conductivity as shown in the figure. The porosity of the sample was 0.46. The permittivity appears to alter from a low-frequency behaviour to a medium-frequency behaviour of  $\omega^{-1.5}$ , roughly at  $\omega = 450, 35, 30$  and  $15 \text{ rad s}^{-1}$  for the different values of liquid conductivity respectively.



**Figure 2.** An approximate equivalent-circuit model for the sample and electrodes used in this paper.

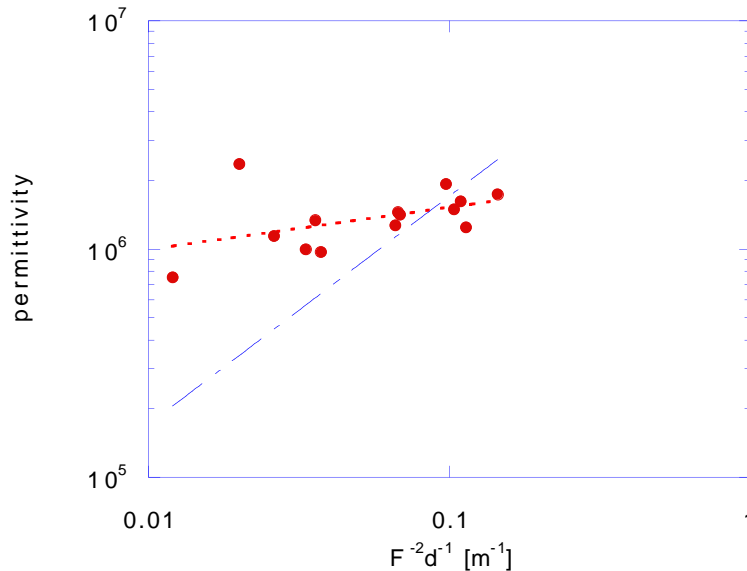
### 3. Electrode polarization: theory versus experiment

In this section we compare experimental data on the low-frequency permittivity with a model assuming polarization effects at the electrodes to be dominant. A so-called Randles circuit is commonly used to describe the dielectric response of electrodes [19]. When the response is dominated by diffusion of ions towards the electrode, the equivalent circuit can be considerably simplified. Our model is based on the circuit in figure 2, where  $W$  is a Warburg impedance, which describes the limitation in current due to ionic diffusion towards an interface. The Warburg impedance has ideally the frequency dependence  $Z_w \propto (i\omega)^{-0.5}$ . In addition,  $C$  is the interfacial capacitance and  $R = Fd/(A\sigma_f)$  is the bulk resistance of the sample. Here  $d$  is the sample thickness,  $A$  the electrode area and  $F$  is the so-called formation factor, which should be defined as [17, 20, 21]

$$F = \lim_{\sigma_f \rightarrow \infty} \frac{1}{\partial \sigma_{app} / \partial \sigma_f}. \quad (1)$$

The formation factor is a measure of the decrease in conductivity of the porous medium, as compared to the conductivity of the pore fluid. The apparent conductivity of a porous material,  $\sigma_{app}$ , is lower than the fluid conductivity because of two effects: parts of the

sample have negligible conductance (the solid) and the conducting paths formed by the pores are not straight but very tortuous.

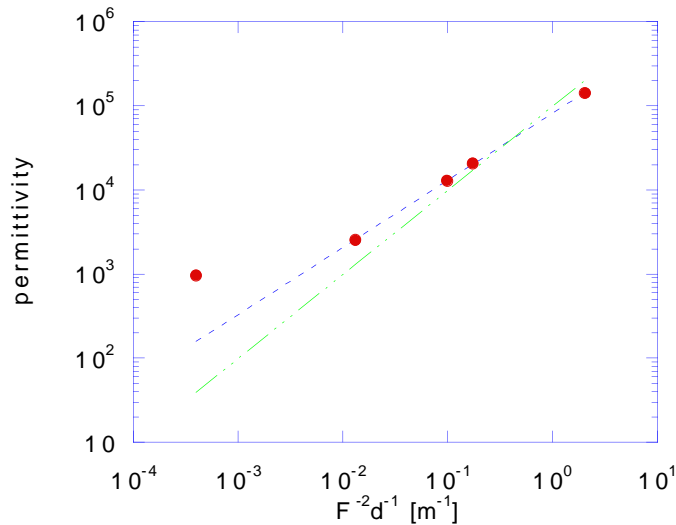


**Figure 3.** The apparent permittivity in our measurements on artificial sandstones as a function of  $F^{-2}d^{-1}$ . The dotted line is a computer fit to a power law (it gives the exponent 0.14) and the chain line is a fit to a proportionality.

The equivalent circuit in figure 2 exhibits the same asymptotic frequency dependence as our experimental data in figure 1, if the Warburg element has a larger admittance than  $C$ . In that case, the circuit capacitance decreases approximately as power laws of frequency, with an exponent  $-1.5$  at high frequencies and an exponent  $-0.5$  at low frequencies.

In order to make a more rigorous comparison between our model and the experimental data, we must also consider the amplitude of the response. It is easily shown that, in the high-frequency region, the capacitance of the circuit in figure 2 is inversely proportional to the square of the bulk resistance. Going over to a description in terms of the apparent permittivity of the sample, we find that the relation  $\epsilon' \propto F^{-2}d^{-1}$  should hold in the region of the high-frequency power law for a set of samples impregnated by the same liquid and using identical electrodes. In figure 3, we show  $\epsilon'$  versus  $F^{-2}d^{-1}$  for our artificial sandstone samples. We have chosen to plot the permittivity values at a reduced frequency value of  $3.3 \times 10^{-6}$ . At this frequency, the data exhibit very high values of the apparent permittivity, and it is in the range where we have an approximate power law with an exponent of  $-1.5$ . It is seen that the correspondence between our model and experiment is poor.

Nøst *et al* [5, 22, 23] have made several measurements of the dielectric properties of brine-filled porous materials made of sintered glass beads. In one of their papers [5], they propose that the high values of  $\epsilon'$  obtained at low frequencies are due to electrode effects. Since Nøst *et al* [5] give numerical values for the formation factors of their samples, we can investigate whether their results show a proportionality between  $\epsilon'$  and  $F^{-2}d^{-1}$ . We took capacitance data for samples of different porosities from figure 3 in reference [5] and then calculated  $\epsilon'$  from the geometrical data provided. In figure 4, we compare those data (at a reduced frequency of  $10^{-6}$ ) with  $F^{-2}d^{-1}$ . The sample with the lowest porosity deviates from the trend, but for the other points, we see a power-law dependence. The best fit



**Figure 4.** The apparent permittivity in the measurements of Nøst *et al* as a function of  $F^{-2}d^{-1}$ . The dotted line is a computer fit to a power law (it gives the exponent 0.8) and the chain line is a fit to a proportionality.

is given by the relation  $\varepsilon' \sim (F^{-2}d^{-1})^{0.8}$ , which is in disagreement with our model for electrode polarization. Note the logarithmic scale; the difference between the prediction of our model and the experimental data can be as large as a factor of two.

It is therefore questionable whether the high values of the permittivity encountered in the cases mentioned here are due to electrode effects. As was mentioned above, another possibility is that these effects emanate at the solid–liquid interface within the porous material. Also in this case, the exponent  $-1.5$  occurs, one example being the case of colloidal suspensions [24, 25].

#### 4. Bulk permittivity and conductivity

In order to establish a relation for the structure dependence of the bulk permittivity, we will argue by analogy with established relations for the bulk conductivity. We therefore first give a brief review of previous results for the dependence of  $\sigma_{app}$  on structural and other parameters. For porous media composed of an inorganic, non-conducting connected matrix where the pores are filled by salty water, the following empirical relation for the DC conductivity has been found [26]:

$$\sigma_{app} = \frac{1}{F} \left( \sigma_f + \frac{A Q_v}{1 + C Q_v / \sigma_f} \right) + E Q_v. \quad (2)$$

Here  $Q_v$  is the amount of the interface charge contribution per unit pore volume,  $A$ ,  $C$  and  $E$  are constants and  $F$  is the formation factor.

For high liquid conductivity, equation (2) shows an approximately linear dependence on  $\sigma_f$ . Johnson *et al* [21, 27] found theoretically for the high- $\sigma_f$  limit

$$\sigma_{app} = \frac{1}{F} \left( \sigma_f + \frac{2\Sigma_s}{\Lambda} \right) \quad (3)$$

where  $\Sigma_s$  is the interface conductivity of the pore walls (in siemens) and the parameter  $\Lambda$  is defined by [21, 27]

$$\frac{\Lambda}{2} = \int |\mathbf{E}_0(\mathbf{r})|^2 dV_p / \int |\mathbf{E}_0(\mathbf{r})|^2 dS. \quad (4)$$

Here  $\mathbf{E}_0$  is the field in the  $\Sigma_s \rightarrow 0$  limit, the integration in the numerator is taken over the pore volume and the integration in the denominator is taken over the pore interface area. The  $\Lambda$  parameter also occurs in an approximate relation between the fluid permeability,  $k$ , and the formation factor [28]:

$$k \approx \frac{\Lambda^2}{8F}. \quad (5)$$

The  $\Lambda$  parameter is a dynamical length, that can be described as an effective-transport pore volume-to-surface area measure. For circular cylindrical pores aligned with the applied field,  $\Lambda$  equals the cylinder radius, and in this case, equation (5) is exact. However, it has been found [28–30] that equation (5) is a good approximation also for more complicated pore geometries, except in the extreme cases when the ‘composite’ is a dilute solution of solid particles in a liquid [30] or when the pores approximate spherical inclusions connected by small, short orifices [29].

It should be noted that conductivity measurements on our samples [17] showed good agreement with equation (3). By combining equations (3) and (5) we could also obtain an estimate of the surface conductivity [17].

At low values of  $\sigma_f$ , Schwartz *et al* [31] obtained another linear dependence between  $\sigma_{app}$  and  $\sigma_f$ :

$$\sigma_{app} = \frac{1}{f} \left[ \Sigma_s + \frac{\sigma_f}{2} \left( \frac{\lambda}{2} + \frac{f}{F} \right) \right]. \quad (6)$$

Here  $\lambda$  is given by an expression analogous to equation (4), by replacing  $\mathbf{E}_0(\mathbf{r})$  by the electric field in the limit where  $\sigma_f \rightarrow 0$ , namely  $\mathbf{e}_0(\mathbf{r})$ . The parameter  $f$  is an analogue of the formation factor, defined in the same limit [31].

At low values of  $\sigma_f$ , the contribution from interface conductivity to the total sample conductivity is  $\Sigma_s/f$ . The corresponding value of this contribution at high values of  $\sigma_f$  is  $2\Sigma_s/(\Lambda F)$ . The ratio,  $K$ , between these two values is directly obtained from expressions given by Schwartz *et al* [31] for  $f$  and  $F$ . We obtain

$$K = \int |\mathbf{e}_0(\mathbf{r})|^2 dS / \int |\mathbf{E}_0(\mathbf{r})|^2 dS. \quad (7)$$

Schwartz *et al* [31] showed that this ratio is highly dependent on the roughness of the interface, but exhibits a weak dependence on porosity, changing from 1.39 at 14.9% porosity to 1.73 at 32.8% porosity for smooth grain surfaces. (For straight cylindrical pores, the ratio becomes unity.)

Since the roughness of the sand grain surface should be similar for all of our samples, we may assume that the value of  $K$  is approximately the same for all samples. Thus, we also neglect any dependence on porosity. For high values of  $\sigma_f$ , the contribution to the apparent conductivity from interface conduction is, according to equation (3),  $2\Sigma_s/(F\Lambda)$ . From the definition of  $K$ , we note that the corresponding contribution at low values of  $\sigma_f$  is  $2K\Sigma_s/(F\Lambda)$ . Between these limits, the contribution from the interface to the apparent conductivity should vary smoothly, and we can write this contribution in the general case as

$$\sigma_{app,ic} = \frac{2c\Sigma_s}{F\Lambda} \quad (8)$$

where  $\Sigma_s$  is an ‘effective interface conductivity’ and  $c$  is a parameter that is unity for high values of  $\sigma_f$  and approaches  $K$  for low values of  $\sigma_f$ . The index  $ic$  is used to denote the contribution from interface conduction. The parameter  $c$  should exhibit a weak porosity dependence and a pronounced dependence on the roughness of the grain surface, at least for high values of  $\Sigma_s$ . As discussed in the introduction, it has been shown [13–15] that the properties of a composite material depend on the properties of the constituents and a characteristic geometric function that takes into account the dependence on microgeometry. The porous materials discussed in this paper may be viewed as three-component materials containing a solid phase, a liquid electrolyte and an interfacial phase. We noted in the introduction that the characteristic geometric function of the composite is the same, for example, for the dielectric constant as for the DC conductivity [13–15]. Thus, the electrical conductivity and the dielectric permittivity should exhibit the same dependence on geometry, and dependences obtained for electrical conductivity should analogously hold for the dielectric permittivity. We assume that the solid material is a perfect insulator; hence, only the conductivities of the liquid and of the interface are contributing to equations (3) and (6). For the permittivity, the situation is different, since all of the components have non-zero permittivity. In the DC case, there will be regions that do not contribute to transport, as there may be pores that are only connected at one end to the rest of the pore system (so-called dead-end pores). In the frequency-dependent case, transport through such pores will not be totally blocked, since the permittivity of the grains (and hence their complex AC conductivity) does not equal zero. However, both the permittivity of the solid ( $\epsilon \approx 4$  for SiO<sub>2</sub>) and of the liquid ( $\epsilon \approx 80$  for water) are several orders of magnitude below the measured  $\epsilon_{app}$  at low frequencies. The admittance of the interface should accordingly be much higher than the admittance of the bulk constituents, and conduction through dead-end pores will be negligible, compared with the conduction along the interfaces of other pores, since the conduction in dead-end pores is restricted by the AC conductivity of the grains.

In analogy to equation (8) we then propose the following relation:

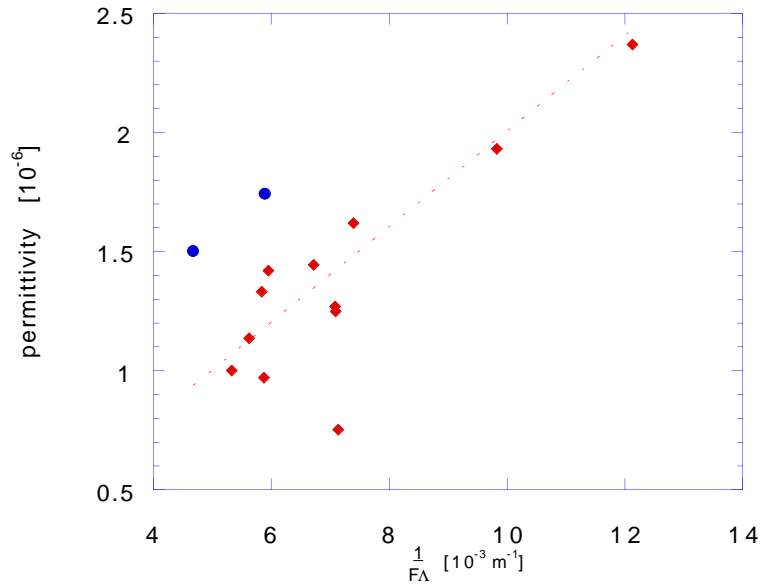
$$\epsilon_{app} = \frac{2cP_s}{F\Lambda} \quad (9)$$

where  $P_s$  is an ‘effective interface permittivity’. It can be inferred from theories on dielectric properties of solid particles in an electrolyte that the electrochemical double layer at the solid–liquid interfaces can give rise to permittivities much larger than bulk values for the solid or liquid [32–34]. This increase can be described by an effective interface permittivity that is in general dependent on frequency and, for a particular frequency, dependent on the ion content of the liquid.

## 5. Comparison of bulk permittivity with experiments

In order to test equation (9) for our artificial sandstone samples, we compared the value of  $\epsilon'$  at a certain frequency with  $1/(\Lambda F)$ —if the proposed relation holds, we should obtain a proportionality. To calculate  $\Lambda$ , we have used equation (5) and the measured values [17] of the fluid permeability and of the formation factor. In figure 5, we depict the measured permittivity as a function of  $1/(\Lambda F)$ . We use the same samples and the same frequency as in figure 3. The agreement with a proportionality is fair, although a few points diverge markedly from the straight line. Actually, some deviations might be explained by the presence of macroscopic inhomogeneities in the samples. The permeability measurements were performed on cores of approximately 4 cm thickness, while the electrical measurements were performed on samples of approximately 5 mm thickness, cut from the cores. Slight

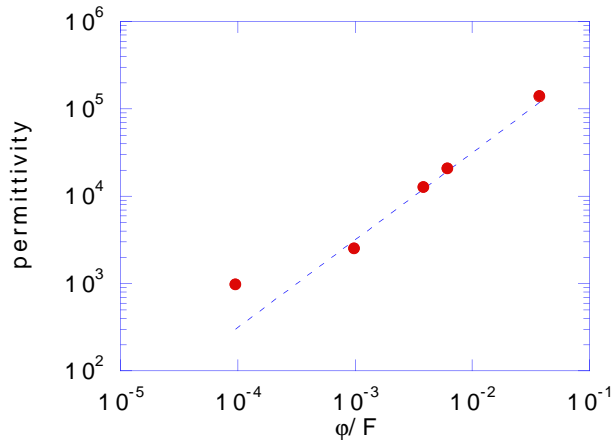




**Figure 5.** The apparent permittivity in our measurements on artificial sandstones as a function of  $1/(\Delta F)$ . The dotted line is a fit to a proportionality. The points denoted by ● show noticeably less deviation from the fit if the empirical relation  $k = 0.013l_g^2F^{-2}$  is used instead of experimental values for  $k$ .

deviations from homogeneity may yield a poor estimate of  $k$  for a particular sample, resulting in an unreliable value of  $\Lambda$ . From reference [17], we see that the relation  $k = Cl_g^2F^{-2}$ , where  $C \approx 0.013$  and  $l_g$  is an average grain size, is approximately valid for our samples. If this relation is used to estimate  $k$ , and thus  $\Lambda$ , a noticeably smaller deviation from the straight line is obtained for the points denoted by circles in figure 5. It should also be mentioned that we have neglected the porosity dependence of  $c$ . Furthermore, we have assumed that all sand grains have equal surface charge, and equal surface roughness, while it is more probable that there are some differences. The effect of the epoxy could also be different among the samples.

We have also compared the results of Nøst *et al* [5] and our proposed relation, equation (9). Their paper does not provide us with enough information to estimate the values of  $\Lambda$ , but in recent articles, Blaschko *et al* [35, 36] have shown that the sintering process changes the pore volume and pore surface in such a way that a simple mathematical relation between them is obtained:  $S = \kappa V^2$ . Here  $\kappa$  is a constant, unique for the specimen used,  $S$  is the pore surface area and  $V$  the pore volume. During sintering, the pore volume decreases and simultaneously the pore surface is transformed from rough to smooth, decreasing the surface area. Since  $\Lambda$  is an ‘effective’ measure of the pore volume-to-surface area ratio, we can estimate  $\Lambda$  by  $V/S$ . It should be remarked that  $\Lambda$  does not equal  $V/S$ , since  $\Lambda$  is a dynamical length related to transport whereas  $V/S$  is a geometric length. However, Schwartz *et al* [30] obtained approximately the same values of  $\Lambda$  and  $V/S$  for simulated packs of spheres of three different sizes, and we can thus assume that  $V/S$  is a fair estimate of  $\Lambda$  (as mentioned above,  $\Lambda$  equals  $V/S$  for cylindrical pores). If the observation of Blaschko *et al* holds, we see that  $V/S$  is inversely proportional to the porosity,  $\varphi$ . Thus, we obtain the result that the permittivity at a given frequency should be roughly proportional



**Figure 6.** The apparent permittivity in the measurements of Nøst *et al* as a function of  $\phi/F$ . The dotted line is a fit to a proportionality.

to  $\phi/F$ .

In figure 6, we show the same permittivity values as in figure 4, plotted as a function of  $\phi/F$ . The agreement with a proportionality is again fair. Still, the data for the lowest porosity deviate somewhat from the trend.

## 6. Conclusions

We have proposed a relation for the low-frequency apparent permittivity of porous solids filled with a liquid. Provided that the high values of the low-frequency permittivity are due to diffusion effects at the pore interfaces, we propose that the permittivity can be approximated by the equation

$$\varepsilon_{app} = \frac{2cP_s}{F\Lambda}$$

where  $P_s$  is an ‘interface permittivity’ that depends on the solid material and on the liquid,  $c$  depends on surface roughness but its dependence on porosity can be neglected, and  $\Lambda$  is a dynamical length. Our measurements on artificial sandstones impregnated with salty water support this relation. We have also shown that it is plausible that the results of Nøst *et al* [5] at low frequencies, for brine-impregnated sintered glass samples, are not due to electrode effects but due to ‘bulk’ polarization at the solid–liquid interface.

## Acknowledgments

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