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An equation for the conductivity of binary mixtures with anisotropic grain structures

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Abstract. An equation is presented which describes the conductivity (resistivity) of a wide variety of binary macroscopic mixtures as a function of the conductivities (resistivities) of the components, the volume (area) fraction of each, and two parameters. Unlike in an earlier version, the granular shape of at least one component is no longer required to be roughly spherical (circular). One parameter is the critical volume (area) fraction. The other, the exponent, is a combination of effective demagnetisation coefficients and the critical fraction. The equation, which is valid for all volume fractions, is shown to fit a variety of experimental data very well. Some deductions about the shape of the grains in the media can be made by analysing the experimental results.

1. Introduction

In a recent paper (McLachlan 1986a), I proposed two equations to describe the conductivity (resistivity) of isotropic binary macroscopic mixtures as a function of the conductivity (resistivity) of the components, the volume fraction of each, the space dimension and a single morphology parameter, that determine a critical volume fraction. These equations are interpolations between Bruggeman's symmetric- and asymmetric-media theories. The symmetric theory is based on a random mixture of spheres and the asymmetric theory on a dispersion of spheres of the one component coated with the other (host) component. Good agreement was found with a wide range of two- and three-dimensional data.

In this paper a more general form of these equations is proposed, which should be valid where neither the grains of the symmetric random medium nor the coated dispersion in the asymmetric media can be characterised by spheres. This equation requires two parameters. The first is the critical volume fraction (f_c) at which a medium, with the same characteristic morphology, but consisting of conducting and insulating components, would undergo a metal–insulator transition (the parameter obviously still has a physical significance when both the components have finite conductivities). The second is an exponent (t) which depends on f_c and a characteristic demagnetisation coefficient for the dispersion. This coefficient depends on the shape of the particles and whether the dispersion is oriented, partially oriented or random. In the case of a 'metal–insulator' mixture, the equation can be put in the same mathematical form as the percolation equation for conductivity. It must however be noted that, unlike the percolation expressions, this equation should be valid at all volume fractions and not only near the metal–insulator transition.

In McLachlan (1986a) and the less general versions given in McLachlan (1985) the equations were all written in terms of a morphology parameter or dimension D and the spatial dimension d, which together determined f_c and the exponent. In this paper it will be shown that a single parameter works because the exponent is a combination of f_c and the fixed demagnetisation coefficient of a sphere ($\frac{1}{3}$ or $1/d$) or a circle ($\frac{1}{2}$ or $1/d$).

In the next section grounds are given for the extension of the equations, used in McLachlan (1985, 1986a), to arbitrary shapes. In a later section the data used in McLachlan (1986a) plus some additional data are fitted using the new equation and the results from this analysis are discussed. The last section contains a brief summary and some conclusions.

2. Theory

Bruggeman's symmetric theory (see Landauer 1978, and the references therein) treats the two (or more) constituents, with conductivities σ_1 and σ_2 and volume fractions f_1 and f_2 on a completely symmetrical basis. The theory, which is based on the expression for the polarisation of a sphere, is for a random mixture of 'spherical' grains of the two constituents, in the correct volume ratio, which together completely fill the media. The case for $d = 1, 2$ and 3 dimensions can be combined in the equation

$$f_1(\sigma_1 - \sigma_m)/[\sigma_1 + (d-1)\sigma_m] + f_2(\sigma_2 - \sigma_m)/[\sigma_2 + (d-1)\sigma_m] = 0. \tag{1}$$

Here σ_m is the conductivity of the medium and if $f_1 = f$, $\sigma_1 = 0$ and $\sigma_2 = \sigma_h$, equation (1) becomes

$$\sigma_m/\sigma_h = [1 - df/(d-1)] = (1 - f/f_c). \tag{1a}$$

Note the metal–insulator transition when the *insulator volume (area) fraction* $f = f_c = d/(d-1)$ i.e. f_c is $\frac{2}{3}$ in three dimensions and $\frac{1}{2}$ in the dimensions. Alternatively for $\sigma_1 = \infty$ or $\rho_1 = 0$ and $1/\sigma_2 = \rho_h$

$$\rho_m/\rho_h = (1 - df') = (1 - f'/f'_c) \tag{1$'a$}$$

where f' *is the conductor volume (area) fraction* and the metal–insulator transition is at $f'_c = 1/d$, which is $\frac{1}{3}$ in three dimensions and $\frac{1}{2}$ in two dimensions.

Bruggeman's asymmetric theory, where the dispersion (conductivity σ_d) consists of an effectively infinite size range of spheres (discs), each of which remains coated with the host constituent (conductivity σ_h) at all volume fractions, is discussed in Landauer (1978, and the references therein) and McLachlan (1985, 1986a). The more general case for oriented ellipsoids, with a demagnetisation coefficient L in the direction of current flow, can be found in Sen *et al* (1981) or in an extensive review of asymmetric theories by Meredith and Tobias (1962). Here the dispersion consists of an infinite size range of oriented ellipsoids (conductivity σ_d) coated at all levels by the host component (conductivity σ_h). This equation can be written as

$$^{1/L}(\sigma_m - \sigma_d)^{1/L}/\sigma_m = (1-f)^{1/L}(\sigma_m - \sigma_h)^{1/L}/\sigma_h \tag{2}$$

When $\sigma_d = 0$, equation (2) becomes

$$\sigma_m/\sigma_h = (1-f)^{1/(1-L)}. \tag{2a}$$

If the conductivity of the ellipsoidal dispersion is much higher than that of the host, equation (2) can be rewritten in terms of the resistivity ($\rho_x = 1/\sigma_x$) and in the limit $\rho_d = 0$, equation (2) becomes

$$\rho_m/\rho_h = (1 - f')^{1/L}. \qquad (2'a)$$

The expressions for dispersions of spheres and discs can be obtained by putting $L = \frac{1}{3}$ and $\frac{1}{2}$ respectively in equations (2), (2a) and (2$'a$). In all these expressions f_c (or f'_c) is equal to one.

For the case of randomly oriented ellipsoids equations (2a) and (2$'a$) can be written as

$$\sigma_m/\sigma_h = (1 - f)^m \qquad (3)$$

or

$$\rho_m/\rho_h = (1 - f')^{m'}. \qquad (3')$$

Values of m and m' have been obtained by evaluating equation (23) in Meredith and Tobias (1962) in the limits σ_d tends to zero and σ_d tends to infinity, respectively. These results are shown in figure 1. This plot is for ellipsoids of rotation with $a \neq b = c$ or $L_a \neq L_b = L_c$ and the aspect ratios given in the figure are c/a. Note that in all cases, except for that of randomly oriented insulating rods, m tends to infinity at the extremes of platelets ($L_c = 0$) and rods ($L_c = 0.5$). Values of m for (3) have also been obtained by Mendelson and Cohen (1982).

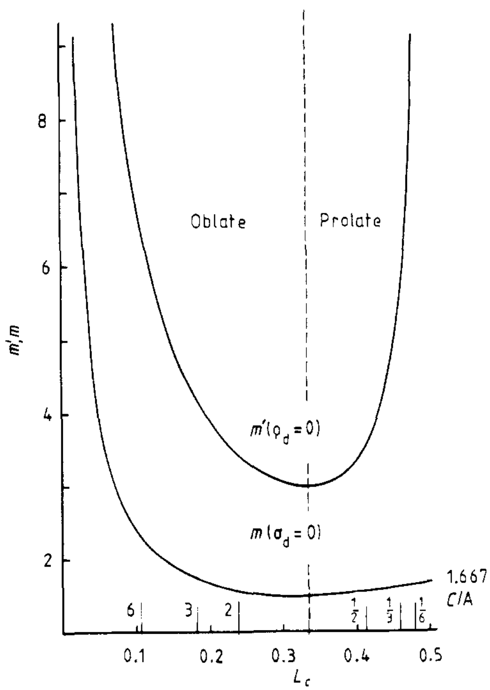

Figure 1. The exponents m and m' for random ellipsoids of revolution plotted against the demagnetisation coefficient $L_c = L_b \neq L_a$. These values are obtained by evaluating equation (23) in Meredith and Tobias (1962) in the limits $\sigma_d = 0$ and $\sigma_d = \infty$.

The expansion for small f or f' of equations (1a), (2a) and (3) or equations (1$'a$), (2$'a$) and (3$'$) are

$$\sigma_m/\sigma_h = 1 - f/(1-L) \qquad \text{and} \qquad 1 - mf \tag{4}$$

or

$$\rho_m/\rho_h = 1 - f'/L \qquad \text{and} \qquad 1 - m'f \tag{4$'$}$$

respectively. These dilute-effective-media expressions are valid for any dilute dispersion of ellipsoids, irrespective of whether the medium will later show a metal–insulator transiton or not.

McLachlan (1985) proposed that the equation

$$\sigma_m/\sigma_h = (1 - f/f_c)^{df_c}/(d-1) \tag{5}$$

(or $(1 - f/f_c)^{f_c/(1-L)}$ for a spherical (or circular) insulating dispersion imbedded in a conducting medium) should hold not only for symmetric and asymmetric morphologies but for all intermediate morphologies. Experimental evidence was presented to show that this equation fitted some experimental data very well. For a perfectly conducting spherical (or circular) dispersion the equation proposed was

$$\rho_m/\rho_h = (1 - f'/f'_c)^{df'_c}. \tag{5$'$}$$

For spheres (3D) and discs (2D) this can be written as $\rho_m/\rho_h = (1 - f'/f'_c)^{f'_c/L}$.

The obvious extensions to equations (5) and (5$'$) for the cases where the dispersions are oriented ellipsoids are therefore

$$\sigma_m/\sigma_h = (1 - f/f_c)^{f_c/(1-L)} \qquad \text{or} \qquad (1 - f/f_c)^t \tag{6}$$

$$\rho_m/\rho_h = (1 - f'/f'_c)^{f'_c/L} \qquad \text{or} \qquad (1 - f'/f'_c)^{t'}. \tag{6$'$}$$

These equations obviously reduce to the symmetric and asymmetric theories for the appropriate values of L, f_c and f'_c. For randomly oriented, ellipsoidal dispersions, equations (3) and (3$'$) can be generalised to

$$\sigma_m/\sigma_h = (1 - f/f_c)^{mf_c} \qquad \text{or} \qquad (1 - f/f_c)^t \tag{7}$$

$$\rho_m/\rho_h = (1 - f'/f'_c)^{m'f'_c} \qquad \text{or} \qquad (1 - f'/f'_c)^{t'}. \tag{7$'$}$$

For small $f(f')$ equations (6) and (7) ((6$'$) and (7$'$)) reduce to equation (4) ((4$'$)) and are therefore rigorously valid in the dilute-effective-media region.

Equations (6) and (7) have the mathematical form of the percolation equation (see for instance Landauer (1978)) and have been shown by McLachlan (1986b) to fit a wide variety of percolation ($\sigma_d = 0$) conductivity results which have inexplicably large critical regimes. The values of L or m, obtained from fitting these results to equations (6) and (7), correspond to what can be expected from the morphologies of the particular medium.

An extended version of equation (6) for the case where both components have finite conductivities and the better conductor is host was given in McLachlan (1986). This is

$$\frac{f(\Sigma_d - \Sigma_m)}{\Sigma_d + [f_c/(1-f_c)]\Sigma_m} + \frac{(1-f)(\Sigma_h - \Sigma_m)}{\Sigma_h + [f_c/(1-f_c)]\Sigma_m} = 0 \tag{8}$$

where $\Sigma_x = \sigma_x^{(d-1)/(df_c)}$. For ellipsoidal dispersions this definition of Σ_x is now replaced by $\Sigma_x = \sigma_x^{1/t}$. This equation obviously reduces to equation (1) for $L = \frac{1}{3}\,(\frac{1}{2})$ and $f_c = \frac{2}{3}\,(\frac{1}{2})$.

It can be shown to be equivalent to equation (2*a*) when $\sigma_d = 0, f_c = 1$ and $L = \frac{1}{3}\,(\frac{1}{2})$. It also reduces to (6) or (7) when $\sigma_d = 0$. This equation should allow one to treat anisotropic systems when $\sigma_h \gg \sigma_d$.

It is interesting to note that the term $f_c/(1-f_c) \equiv (1-f'_c)/f'_c$ in (8) has been shown by Leath (1976) to be the limit, for an infinite system, of the surface to volume (perimeter to surface) ratio at or near the percolation threshold, or f_c in this case. This implies that, at least in some systems, there is a relationship between $f_c(f'_c)$ and the fractal dimension. Effective-media theory for binary resistor networks gives (1) with $(d-1)$ replaced by $\frac{1}{2}Z - 1$ where Z is the number of bonds at each node of the network (Yonezawa *et al* 1981, Kirkpatrick 1971). In (8), which is a continuum formula, $\frac{1}{2}Z - 1$ should probably be replaced not by the average number of contacts between the *conducting* 'grains' but by the number of contacts multiplied by their areas i.e. an effective contact area per unit volume fraction. This concept is best illustrated at the extremes. For an asymmetric insulator host medium $f'_c = 1$ and $(1-f'_c)/f'_c = 0$ (i.e. zero effective contact area between the conducting grains for $f' \neq 1$) while for an asymmetric conductor host medium $f_c = 1, f'_c = 0$ and $(1-f'_c)f'_c = \infty$ (i.e. an effectively infinite contact area per unit volume for the continuous conducting host component with embedded isolated insulating grains for $f \leqslant 1$).

Equation (8) also implies that the symmetric effective-media equation ($t = 1$) for random ellipsoids is

$$f_1(\sigma_1 - \sigma_m)/\{\sigma_1 + [(1-L)/L]\sigma_m\} + f_2(\sigma_2 - \sigma_m)/\{\sigma_2 + [(1-L)/L]\sigma_m\} = 0. \tag{9}$$

While this is true for $L = \frac{1}{3}$ (3D) and $\frac{1}{2}$ (2D) and also for $L = 0$ and 1 (if written in terms of ρ_1, ρ_2 and ρ_m), this has not been proved in general. For very small f_1 or f_2, equation (9) gives the same values for σ_m as the Cohen *et al* (1973) version of the Clausius–Mossotti relationship for ellipsoidal cavities.

In McLachlan (1985, 1986a) all the equations are written in both the conductor host ($\sigma_h > \sigma_d$; $0 < f_c \leqslant \frac{2}{3}$ for 3D) and resistor host ($\rho_h > \rho_d$; $0 < f'_c \leqslant \frac{1}{3}$ for 3D) versions using a morphology parameter D ($f_c = (d-1)/D$ and $f'_c = 1/D$). This was necessary in order to keep $D \leqslant d$, which is essential if D is to have any significance as a dimension, fractal or otherwise. Here the morphology parameter D determined the metal–insulator transition composition for a system where the dispersion could be characterised by an effective N of $\frac{1}{3}\,(\frac{1}{2})$ if oriented and an m of 1.5 (2) if random. The one-parameter equations work remarkably well, possibly because $1.5 \leqslant m \leqslant 1.67$ for many randomly oriented ellipsoidal systems (figure 1).

Equation (8) may also be written in the form

$$\frac{f(P_m - P_d)}{P_m + [(1-f'_c)/f'_c]P_d} + \frac{(1-f)(P_m - P_h)}{P_m + [(1-f'_c)/f'_c]P_h} = 0 \tag{8$'$}$$

where $P_x = \sigma_x^{1/t'}$. This equation reduces to equations (1′*a*), (2′*a*), (6′) or (7′) in the appropriate limits and may be obtained directly from equation (8). The data, where both σ_h and σ_d (or ρ_h and ρ_d) are finite, treated in the next section show that either (8) or (8′) may be used. The same values of t, t' and $f_c/(1-f_c) \equiv (1-f'_c)/f'_c$ are obtained in all cases. As it is not intuitively obvious that t is always equal to t' they have until now been treated as different parameters. In all the media examined t is found equal to t', so henceforth they will be taken to have the same value i.e. $t = t'$. Therefore, except where $\sigma_d = 0$ or $\rho_d = 0$, the choice of equations is somewhat arbitrary. An examination of (6) and (6′) shows that in order to find the effective L of the insulating dispersion in the low-insulator-fraction region, $t = f_c/(1 - L)$ and to get the effective L' of the conducting dispersion in the low-conductor-fraction region, $t = f_c'/L'$. Equations (8) and (8′) may also be written as quadratic equations and solved directly for σ_m or ρ_m. Examples of the mathematical form of (8) when plotted as σ_m against $|f_c - f|$ are given in the next section. This emphasises the undoubted validity of effective-media theory in both (f and f') dilute limits.

Equations (8) and (8′) should also apply to dielectric, magnetic permeability, thermal conductivity and gaseous diffusion experiments.

3. Experimental evidence

3.1. General remarks

As (8) and (8′) presented in the previous section are, except at certain extremes, phenomenological, they are justified by comparison with experiment in this section. Other than for the bismuth film, which was measured in the author's laboratory, the data are digitised from enlargements of the graphical data presented in the literature. The computer uses the experimental (conductivity) resistivity and variable parameters to calculate an area or volume fraction, called fit, from (8) or (8′). Fit is then compared with the given (or calculated) area or volume fraction (Frn) and the quantity $\chi^2 = \Sigma_N[(\text{Fit-Frn})/0.01]^2$ is minimised by the program by varying the non-fixed parameters. If $\delta = [\chi^2/(N - P)]^{1/2} = 1$, where N is the number of experimental points and P is the number of variable parameters, it is claimed that data have been fitted to an accuracy of 0.01 in the area or volume fraction. δ and the errors given with the fitted parameters in the text are calculated by the program. A single value of the conductivity of each component is sufficient to fit the data with $\delta \leqslant 1.6$ and no composition- or size-dependent conductivities are necessary, as was the case in McLachlan (1986a).

In the next section the results of fitting the data with one parameter ($f_c = (d - 1)/D$ or $f_c' = 1/D$ and $\Sigma_x = \sigma_x^{1/t}$ where $t = df_c/(d - 1) = d/D$ or $P_x = \rho_x^{1/t}$ where $t = df_c' = d/D$), as was done in McLachlan (1986a), are given first. (All these results are for composition- or size-independent σs or ρs). These data are not discussed but can be compared with the results from a two-parameter fit. Note that the gold and bismuth films are 'two-dimensional' systems.

The results for the two-parameter fits using (8) or (8′) are given after those for one-parameter fits. All the parameters, other than for the nickel–vanadium oxide composite, are given as f_c', t and resistivities. The parameters obtained using (8) and (8′) are always related to each other by $f_c' + f_c = 1$, $\rho_d = 1/\sigma_d$, $\rho_h = 1/\sigma_h$, $t = t'$ and the δ values are found to be the same. Note f and f_c are the fractions for the more resistive ('insulating') component (σ_d or σ_h) and f' and f_c' are the fractions for the less resistive ('conducting') component (ρ_h or ρ_d). The values of L ('insulator' particles) and L' ('conductor' particles) are calculated from the formulae $L = 1 - f_c/t$ and $L' = f_c'/t$. It should be noted that in an asymmetric medium with the conductor as host $f_c = 1, f_c' = 0$ and $L' = 0$ (i.e. the current (or flux) will always remain in the host sponge for $\sigma_d = 0$). In an asymmetric medium with the insulator as host $f_c' = 1, f_c = 0$ and $L = 1$ (i.e. the current (or flux) tries to avoid the continuous sponge for $\rho_h \gg \rho_d$). m and m' are found from $m = t/f_c$ and $m' = t'/f_c'$. Note L and m are characteristic for the insulating dispersion in the low-f limit and L' and m' of the conducting dispersion in the low-f' limit.

As, unless one component has an immeasurably low conductivity ($\sigma_d = 0$) or resistivity ($\rho_d = 0$), either (8) (with $\sigma_h > \sigma_d$) or (8′) (with $\rho_h > \rho_d$) can be used, the results are graphed in the form σ_m against $|f_c - f|$. The immediate striking feature, for media where the ratios of the component conductivities (resistivities) are large, will be seen to be the straight line regions near *each* end of the composition range. The intercept of the two lines will be found to be opposite the conductivity of the medium when $f = f_c$. When the ratio is very large ($\sigma_h \gg \sigma_d$) the slope of both lines is found to be close to the given value of t but decreases rapidly as the values of the conductivities approach each other.

3.2. *Details of results*

The experiments of Laibowitz *et al* (1983) on the resistivity as a function of the directly measured area fraction for gold films provide a good starting example of a two-dimensional system. The one-parameter fits are $\delta = 1.8$, $f_c' = 0.763 \pm 0.001$, $t = 1.52 \pm 0.001$, $\rho(\text{gold}) = 8.3 \pm 0.01\ \Omega$, $\rho(\text{substrate}) = (1.8 \pm 0.1) \times 10^7\ \Omega$. The two-parameter fits are $\delta = 1.0$, $f_c' = 0.755 \pm 0.008$, $t = 1.75 \pm 0.17$, $\rho(\text{gold}) = 6.6 \pm 2.0\ \Omega$, $\rho(\text{substrate})$ $(2.8 \pm 1.5) \times 10^7\ \Omega$, $L = 0.86 \pm 0.09$, $L' = 0.43 \pm 0.05$, $m = 7.1 \pm 0.7$ and $m' = 2.3 \pm 0.3$.

The raw data for the bismuth film consisted of the resistance between two gold pads on a glass substrate, as a function of time, measured during the formation of an ion-beam-sputtered bismuth film. Liang *et al* (1976) performed a similar experiment on evaporated bismuth films, but show no data between 10^9 and $10^4\ \Omega$ as their resistive transition was too rapid to observe. Their transition occurred at about 90 Å and using an electron micrograph they estimated the area fraction at this crossover point to be 0.67. They determined their other area fractions from the formulae $X = 1 - \exp(-N_n r^2)$ and effective thickness $= (\frac{4}{3})N_n r_n^3$ with N_n adjusted to give $X = 0.67$ at their critical effective thickness (90 Å). The area fractions for bismuth were therefore determined from the formula.

$$X = 1 - \exp[-N_a(\text{rate} \times \text{time})^{2/3}]$$

where N_a is a variable parameter.

For the one-parameter fit it was found (McLachlan 1986a) that in order to get physically meaningful results f_c' had to be fixed. The value of $f_c' = 0.667$, as determined by Liang and co-workers, was found to give reasonable results for both one- and two-parameter fits. These are $\delta = 0.47$, $f_c' = 0.667$, $t = 1.33$, $\rho(\text{bismuth}) = 3358 \pm 15\ \Omega$ and $\rho(\text{substrate})$ $(1.6 \pm 0.3) \times 10^9\ \Omega$ and $\delta = 0.34$, $f_c' = 0.667$, $t = 1.88 \pm 0.05$, $\rho(\text{bismuth}) = 185 \pm 15\ \Omega$, $\rho(\text{substrate}) = (1.44 \pm 0.02) \times 10^{11}\ \Omega$, $L = 0.82 \pm 0.02$, $L' = 0.354 \pm 0.009$, $m = 5.7 \pm 0.1$, $m' = 2.8 \pm 0.1$ and $N_a = 0.084$ Å^{-2}. However for the two-parameter formula a second, statistically better, fit was found when N_a and f_c were allowed to vary. These values are $\delta = 0.27$, $f_c' = 0.798 \pm 0.002$, $t = 2.04 \pm 0.21$, $\rho(\text{bismuth}) = 287 \pm 40\ \Omega$, $\rho(\text{substrate}) = (4.9 \pm 4.0) \times 10^{11}\ \Omega$, $L = 0.90 \pm 0.04$, $L' = 0.39 \pm 0.04$, $m = 10.1 \pm 0.4$, $m' = 2.5 \pm 0.3$ and $N_a = 0.123$ Å^{-2}. Using a model where all the initially evaporated material in a given area goes to form a hemisphere, together with the computer determined values of $N_a = 0.084$ Å^{-2} ($f_c = 0.667$) and 0.123 Å^{-2} ($f_c = 0.798$), these areas are found to be 11 900 Å^2 and 3800 Å^2 respectively. This leads to characteristic structure sizes of 109 Å and 62 Å which is what is observed for many soft-metal films. These are somewhat smaller than Liang *et al* (1976) value of 200 Å but it is well known that ion-beam sputtering produces smaller crystallites than evaporation. Plots of the two-dimensional data are shown in figure 2.

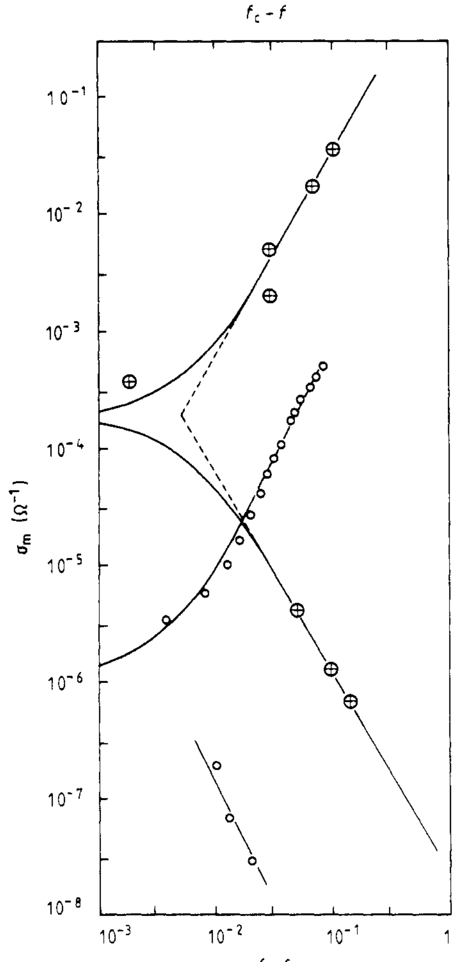

Figure 2. The conductivity of a gold (⊕) and a bismuth (○) film as a function of $f_c - f$ on the upper 'conducting' side and $f - f_c$ on the lower 'insulating' side. f is the non-coated area fraction and f_c the critical value ($f_c = 0.245$ (gold) and 0.202 (bismuth)). The full curves are equation (8) using the parameters given in the text. The broken lines are extrapolations from the dilute linear (or power law) linear regions.

An evaluation of m or m' in two dimensions does not exist but the minimum values of m and m' are certainly 2. The values of $m' = 2.3$ to 2.8 therefore correspond to random prolate ellipses, as most micrographs of evaporating films show prolate-shaped metallic islands. Because there is no reason to believe the metal particles should not be randomly oriented, no analysis is made in terms of L and L'. Note that in this model a finite sheet resistivity for the surface of the substrate (Si_3N_4 for the gold and glass for the bismuth) is postulated.

The data of Smith and Anderson (1981) for a thick arc-sprayed film of Ni ($\sigma = 5565$ $(\Omega\,\mathrm{cm})^{-1}$) and V_2O_5 ($\sigma = 0.485$ $(\Omega\,\mathrm{cm})^{-1}$), in which there are only one or two variable parameters, gives the following results: $\delta = 2.1$, $f_c = 0.826 \pm 0.007$, $t = 1.24 \pm 0.01$. $\sigma(\mathrm{Ni}) = 5565$ $(\Omega\,\mathrm{cm})^{-1}$, $\sigma(V_2O_5) = 0.485$ $(\Omega\,\mathrm{cm})^{-1}$ and $\delta = 1.6$, $f_c =$

0.884 ± 0.015, $t = 1.44 \pm 0.1$, $\sigma(\mathrm{Ni}) = 5565$ $(\Omega\,\mathrm{cm})^{-1}$, $\sigma(V_2O_5) = 0.485$ $(\Omega\,\mathrm{cm})^{-1}$, $L = 0.416 \pm 0.045$, $L' = 0.108 \pm 0.013$, $m = 1.7 \pm 0.2$ and $m' = 9.2 \pm 1.1$. Smith and Anderson (1981) remark that 'the deposited particles tend to form platelets' so the oriented interpretation is probably correct for their results. The value of $L = 0.416$ indicates slightly oblate V_2O_5 particles with the nickel particles partially wrapped around them at the metal-rich end; which is a conductor-host-type situation. An L' of 0.108 indicates that for small volume fractions of nickel, nickel threads or platelets, with their axis perpendicular to the net current direction, play a significant role. The results are plotted in figure 3.

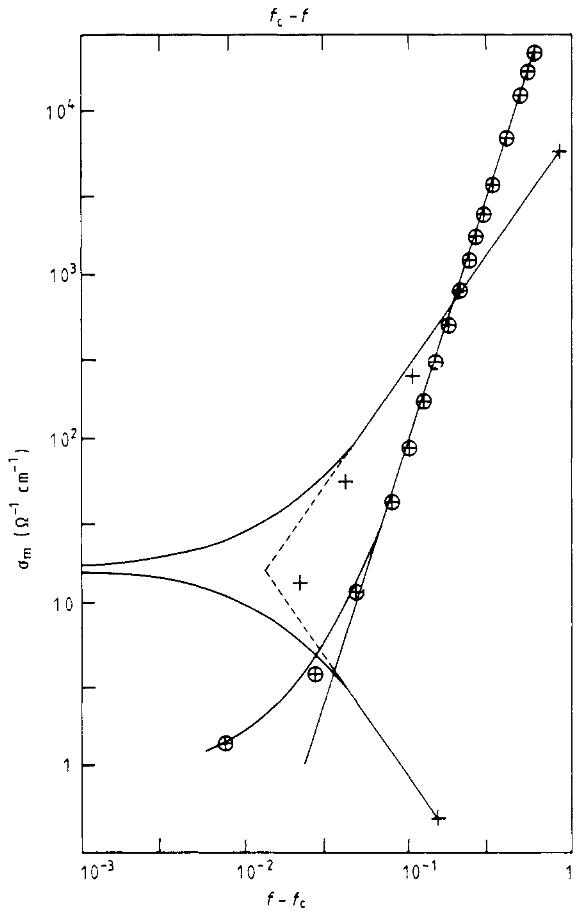

Figure 3. The conductivity of an arc sprayed Ni–V_2O_3 film (+) and a sputtered W–Al_2O_3 film ($\oplus$) as a function of $f_c - f$ on the upper 'conducting' side and $f - f_c$ on the lower 'insulating' side. f is the insulator volume fraction and f_c the critical value ($f_c = 0.844$ for Ni–V_2O_3 and 0.586 for W–Al_2O_3). The full curves are equation (8) using the parameters given in the text. The broken lines are extrapolations from the dilute linear (or power law) linear regions.

The tungsten–alumina cermet systems analysed in McLachlan (1986a) are re-analysed with some interesting results. The as-prepared tungsten–alumina system (Abeles *et al* 1975) fits (8′) remarkably well. The parameters are $\delta = 3.4$, $f_c' =$

0.474 ± 0.007, $t = 1.42 \pm 0.02$, $\rho(W) = (4.1 \pm 0.2) \times 10^{-5}$ Ω cm, $\rho(Al_2O_3) = (1.0 \pm 2.0) \times 10^9$ Ω cm and $\delta = 0.24$, $f_c' = 0.424 \pm 0.004$, $t = 3.14 \pm 0.08$, $\rho(W) = (4.53 \pm 0.04) \times 10^{-5}$ Ω cm, $\rho(Al_2O_3) = (1.0 \pm 0.4) \times 10^4$ Ω cm, $L = 0.82 \pm 0.01$, $L' = 0.135 \pm 0.02$, $m = 5.5 \pm 0.1$ and $m' = 7.4 \pm 0.1$. The results are plotted in figure 3. The calculated values of $L = 0.819$ and $L' = 0.135$ indicate that there is no clear host and dispersion component but that the medium consists of interpenetrating matrices of plates and threads. This is why the one-parameter fit is so poor. However, the as-prepared W–Al_2O_3, if it shows no orientation effects due to sputtering onto a plane surface, is probably a random medium. As $m = 5.5$ for the insulating particles this corresponds to random alumina platelets in tungsten-rich media but $m' = 7.4$ could correspond to *plates or threads* of tungsten in an alumina-rich media. $m' = 7.4$ corresponds to an aspect ratio of $\frac{1}{5}$ for threads or about 7 for platelets. All Abeles *et al* (1975) say is that the grains in the as-prepared film are less than 20 Å. This probably means that their shape was not or could not be determined. This conjecture is somewhat speculative as the data analysed come from the tungsten-rich side.

The annealed tungsten–alumina samples give $\delta = 2.1$, $f_c' = 0.474 \pm 0.002$, $t = 1.421 \pm 0.006$, $\rho(W) = (8.2 \pm 0.1) \times 10^{-6}$ Ω cm, $\rho(Al_2O_3) = (1.0 \pm 1.6) \times 10^9$ Ω cm and $\delta = 1.0$, $f_c' = 0.484 \pm 0.005$, $t = 1.36 \pm 0.06$, $\rho(W) = (7.7 \pm 0.3) \times 10^{-6}$ Ω cm, $\rho(Al_2O_3) = (1.0 \pm 0.7) \times 10^4$ Ω cm, $L = 0.626 \pm 0.034$, $L' = 0.355 \pm 0.02$, $m = 2.7 \pm 0.15$ and $m' = 2.8 \pm 0.15$. This clearly indicates nearly spherical metal spheres ($L' = 0.355$) surrounded by a non-continuous sponge or jointed platelets. The spherical metal particles, which appear after annealing, are clearly shown in a photograph given in Abeles *et al* (1975). At low insulator concentrations the alumina would appear to be platelets embedded in tungsten ($L = 0.63$).

Finally, two emulsions (Meredith and Tobias 1961), where the given ratio of the resistivities of the components is not very large, are analysed and plotted in figure 3. For the ratio 15.7 emulsion the parameters are $\delta = 3.5$, $f_c' = 0.48 \pm 0.01$, $t = 1.42 \pm 0.03$, $\rho(\text{host})/\rho(\text{disp}) = 15.7$ and $\delta = 0.42$, $f_c' = 0.536 \pm 0.005$, $t = 1.63 \pm 0.1$, $\rho(\text{host})/\rho(\text{disp}) = 15.7$, $L = 0.72 \pm 0.01$, $L' = 0.328 \pm 0.046$, $m = 3.5 \pm 0.05$ and $m' = 3.0 \pm 0.4$. For the ratio 101 emulsion the parameters are $\delta = 5.0$, $f_c' = 0.45 \pm 0.07$, $t = 1.35 \pm 0.2$, $\rho(\text{host})/\rho(\text{disp}) = 101$ and $\delta = 0.89$, $f_c' = 1.00 \pm 0.04$, $t = 3.7 \pm 0.08$, $\rho(\text{host})/\rho(\text{disp}) = 101$, $L = 1.00 \pm 0.06$, $L' = 0.267 \pm 0.016$, $m = \infty$ and $m' = 3.7 \pm 0.2$. (There is also a two-parameter minimum near the one-parameter values with $\delta = 3.2$, $f_c' = 0.57 \pm 0.07$, $t = 1.2 \pm 0.1$.) The single-parameter results are very poor in both cases. The δs from the two-parameter fits are well within the expected inaccuracies. The first ($\rho_h/\rho_d = 15.7$) indicates emulsified spherical particles ($L' \approx 0.33$) of the more conducting component which come into continuous contact at a volume fraction of 0.536. This could be indicative of the phase inversion (host to dispersion and vice versa) which occurs at higher emulsion (dispersion) fractions (Meredith and Tobias 1961). The two-parameter fit of the emulsion with a conductivity ratio of 101 indicates random slightly prolate ellipsoidal conducting particles ($m' = 3.7$) surrounded at all volume fractions by the more insulating component. This result shows no sign of the phase inversion previously mentioned but the experiments do not go to quite so high a volume fraction of emulsion as for the previous (ratio 15.7) sample. Both results are plotted in figure 4; also shown are the lines with slope t and $-t$ going through the extreme composition points of $f = 0$ and 1. The intercept is again opposite the conductivity at $f = f_c$.

Figure 1 shows the inability of effective-media theory to distinguish between random conducting oblate and prolate ellipsoids in an insulating host. This has dramatic

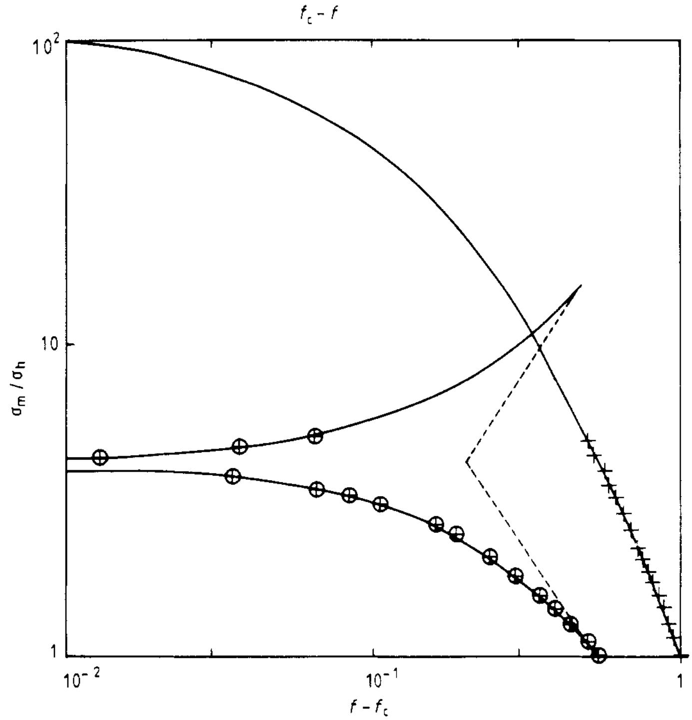

Figure 4. The relative conductivity of two emulsions $\sigma_d/\sigma_h = 15.7$ (⊕) and σ_d/σ_h (+) plotted as a function of $f_c - f$ on the upper 'conducting' side and $f - f_c$ on the lower 'insulating' side. f is the insulator (σ_h component) volume fraction and f_c the critical value ($f_c = 0.464$ for the first and 0 for the second emulsion). The full curves are (8) using the parameters given in the text. The broken lines are extrapolations from the dilute linear (or power law) linear regions using the derived value of t.

consequences in models for the conductivity of rocks. The most commonly used equation to characterise the conductivity of rock formations, is a modified Archie's law $\sigma_m/\sigma_w = a\varphi^t$ where σ_w is the conductivity of the ground water, φ the porosity or water conduction fraction $(1 - f = f')$, t is called the cementation index and a is a constant of the order of unity. (See for instance Keller and Frischknecht 1966.) The results for sandstones and other consolidated rocks fit this equation in a semi-quantitative way (see for instance Keller and Frischknecht 1966). Many attempts to justify this equation start from the asymmetric conductor host situation, visualising a situation like unconsolidated sand surrounded by water ($\varphi \approx 0.3$). The decrease in σ_m with φ and the lack of φ_c (f'_c) in the asymmetric model implies that sheets of water coat the rock grains for all $\varphi > 0$. This is obviously a most unsatisfactory model for consolidated or cemented rocks. If, however, one assumes an undetectably small φ_c or f'_c (say 0.001 to 0.01) together with a t of about 2 (Keller and Frischknecht 1966), an equally valid interpretation of the low results is a highly insulating rock component penetrated by randomly oriented threads of ground water. $m' = t/f'_c$ for the threads is then in the range 200 to 2000 corresponding to an L_c from about 0.4992 to about 0.49992 (L_a (along the axis) ≈ 0.0016 to 0.00016). This corresponds to 'length to diameter' ratios in the range 200 to 1000 for extremely low values of φ. As the rock grains, in a highly consolidated medium, are cemented together over most of their surface area, this model is obviously more correct than the water-coated grains of a conductor host asymmetric-media theory. In fact it is the only way that an effective-media model can correspond to the real situation in consolidated media.

Preliminary results using (8) or (8′) to analyse the magnetic permeability of mixtures are given next. The two-parameter results for a sample consisting of insulator-coated permalloy flakes (Veinberg 1967) are $\delta = 1.50$, $f_c' = 1.0$, $t = 21.4$ and $m' = 21.4$. The permeability of the pure permalloy was given as 1287 and the permeability of the insulator was taken as 1. These results correspond perfectly to the known morphology of the system. Cemented tungsten carbide–cobalt is a commercial drilling and cutting product in which the WC grains are cemented together by the Co. The lowest volume fraction of Co used commercially is about 0.1 and photo-micrographs show these and higher-volume-fraction specimens to consist of WC grains interspersed by Co layers and lumps. Magnetic susceptibility results (McLachlan and White 1987) in the 0.1 to 0.27 Co volume fraction range were analysed and gave $\delta = 0.74$, $f_c'(\mathrm{Co}) = 0.088$, $t = 0.436$ and $m' = 4.95$. The permeability of the Co (contaminated with W and C) is found to be 25.6 and that of the WC grains was fixed at 1. These parameters correspond to the observed morphology of magnetic Co layers coating the WC grains. According to this analysis the Co layers become interconnected at 0.088 volume fraction Co. A more extensive publication of these and other magnetic susceptibility results is to be published (McLachan and White 1987).

4. Discussion

The semi-phenomenological equations (8) and (8′) have been shown to fit a surprising variety of two- and three-dimensional experimental data. In many cases the total error is well within the original experimental error plus the inherent errors in digitising the data. This success is also surprising because in many instances the systems do not have a very wide range of differently sized grains, so that theories based on scaling should not strictly apply. Milton (1984) has shown that (1) should be valid if the size range of the grains of components 1 and 2 is very large. The derivation of (2) implies a nearly infinite size range of the dispersion spheres. This is emphasised in the more modern derivation of Sen *et al* (1981) who also arrive at (3). Nonetheless it is very useful to have an equation such as (8) (or (8′)) which accurately fits such a wide variety of data and from which qualitative data regarding the shape of the particles can be obtained.

The amount of information against which (8) and (8′) are tested is not extensive and further experiments should be analysed in order to ascertain exactly how well and under what constraints these equations fit the data. It is also very gratifying that a single exponent (t) appears to fit the data on both sides of the critical composition in the few cases where this could be tested. This too should be further investigated.

It may well be argued that in all cases, except where f_c and f_c' are one, the host and dispersion cannot be clearly distinguished because for very small values of f the conductor is host but for values of f very close to one the insulator plays the role of host and vice versa. The difference between host and dispersion is however always clearly distinguished if one component is either a perfect insulator or perfect conductor. The equations may be used in the context that in (8) $\sigma_h > \sigma_d$ and in (8′) $\rho_h > \rho_d$.

As previously stated (8) and (8′) should apply to dielectric constant, magnetic permeability, electrical conductivity and thermal conductivity as well as gaseous diffusion experiments. In this paper the equations have been primarily tested using electrical conductivity experiments but preliminary results for magnetic susceptibility measurements have also been given. An application for gaseous diffusion is mentioned in McLachlan (1986). Further experiments to test the validity of these ideas are being carried out in the author's laboratory.

References

Abeles B and Hanak J J 1971 *Phys. Rev.* A **34** 165

Abeles B, Pinch H L and Gittleman J I 1975 *Phys. Rev. Lett.* **35** 247

Cohen R W, Cooly G D, Coutts M D and Abeles B 1973 *Phys. Rev.* B **8** 3689

Keller G V and Frischknecht F G 1966 *Electrical Methods in Geophysical Prospecting* (Oxford: Pergamon) p 22

Kirkpatrick S 1971 *Phys. Rev. Lett.* **27** 1722

Laibowitz R B, Voss R F and Allessandrini E I 1983 *Percolation, Localisation and Superconductivity, Nato Advanced Study Inst.* Series B, vol 109, ed. A M Goldman and S A Wolf (New York: Plenum) p 145

Landauer R 1978 *Electrical Transport and Optical Properties of Inhomogeneous Media* (Am. Inst. Phys. Conf. Proc. 40)

Leath P L 1976 *Phys. Rev. Lett.* **36** 921

Liang N T, Yueh Shan and Shou-yik Wang 1976 *Phys. Rev. Lett.* **37** 526

McLachlan D S 1985 *J. Phys. C: Solid State Phys.* **18** 1891

—— 1986a *J. Phys. C: Solid State Phys.* **19** 1339

—— 1986b *Solid State Commun.* **60** 821

McLachlan D S and White H 1987 *J. Magn. Magn. Mater.* to be published

Mendelson K S and Cohen M H 1982 *Geophysics* **47** 257

Meredith R E and Tobias C W 1961 *J. Electrochem. Soc.* **108** 286

—— 1962 *Advances in Electrochemistry and Electrochemical Engineering* vol 2, ed. C W Tobias (New York: Interscience) p 15

Milton G W 1984 *Physics and Chemistry of Porous Media* (New York: Am. Inst. Phys.) p 66

Sen P N, Scala C and Cohen M H 1981 *Geophysics* **46** 781

Smith D P H and Anderson J C 1981 *Phil. Mag.* B **43** 811

Veinberg A K 1967 *Sov. Phys.-Dokl.* **11** 593

Yonezawa F, Webman I and Cohen M H 1981 *Anderson Localisation* ed. Y Nagavka and H Fukuyama (Berlin: Springer) p 166