Electrostatic charging of a fractal cluster and variable-range hopping in thin discontinuous metal films

LETTER TO THE EDITOR

Electrostatic charging of a fractal cluster and variable-range hopping in thin discontinuous metal films

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Abstract. It is argued that the capacitance of a fractal metallic cluster scales with its size as $C \sim r^c$, where $0 < c < 1$ is a new charging exponent. A new dimension d_c is defined to characterise the electrostatically unshielded surface of the cluster. In effect, $c = 2 - d + d_c$ is obtained, where d is Euclidean dimension. Based upon this, and using cluster-size distribution from percolation theory, it is shown that the temperature dependence of the variable-range-hopping conductivity of discontinuous metal films is given by $\ln \sigma \propto -1/T^x$ with $x = 1/(1 + c)$. The value of x is predicted to lie in the range $\frac{1}{2}$–1, in close agreement with experiments. It is suggested that the cermet conductivities, which have $x = \frac{1}{2}$, can also be explained within the framework of the present arguments.

Thin metal films are discontinuous during early stages of their formation (typically below 100 Å). They consist of isolated metallic islands distributed randomly in space. With increasing thickness, the islands grow and coalesce until, at a critical thickness, a continuous metallic path is established. The transition from insulating to metallic character at the threshold is a critical transition, and is very well described by percolation theory [1–4]. Metal–insulator composite materials (called cermets) also exhibit a similar type of metal–insulator transition. In the insulating regime, the low-field DC conductivity of these systems exhibits a temperature dependence of the form

$$\ln \sigma \propto -1/T^x \tag{1}$$

over a large temperature range ($2\,\text{K} < T < 300\,\text{K}$). The temperature exponent $x \lesssim 1$ holds for discontinuous films and $x = \frac{1}{2}$ for cermets [5–8]. Considerable effort has been made in the past to explain the cermet behaviour [5–13]. Some theories do predict an $x = \frac{1}{2}$ dependence, although there is no unanimity in the basic arguments [6, 9, 12, 13]. This Letter is primarily concerned with the conductivity behaviour of discontinuous films, which is least understood so far, though in several respects it is similar to that of cermets. In addition, it is suggested that the cermet behaviour can follow as a special case of the general considerations here.

It is generally accepted that the basic physics of conduction is essentially the one originally outlined by Nuegbauer and Webb [5]. According to their model, in thermal equilibrium a fraction of the metal islands are charged either by loosing or gaining an electron to or from a neighbouring, initially neutral, island. The charge transport occurs by thermally activated tunnelling from charged to neutral islands. Thermal activation is required because of the non-negligible energy change associated with the electrostatic

charging of metal islands during tunnelling. The charging energy of an island, $E_c = e^2/2C$, where C is its capacitance. In the past, it has invariably been assumed that the island capacitance, C, is proportional to its size r, i.e. $C \sim r$. This is certainly correct for metal particles having regular surface morphology. But for worm-like metal islands (clusters), typical of discontinuous films, this may be in gross error. In the following we first examine this point.

It is now well known that the metal clusters near a metal–insulator transition are self-similar fractals, with tortuous morphology. Percolation theory describes their behaviour well [1–4]. It is therefore pertinent to ask, how does the capacitance (and hence the charging energy) of a fractal cluster scale with its size? Consider the perimeter structure of a ramified (stringy) fractal cluster. It consists of a large number of 'burrows' or 'invaginations' (see micrographs of Voss and co-workers [1]). The perimeter, t, of such a cluster is proportional to its area, s. The area scales with RMS radius r as $s \sim r^{d_f}$, therefore, $t \sim r^{d_f}$ where d_f is the fractal dimension of an individual cluster boundary (for Euclidean shapes of dimension d, $d_f = d - 1$). If a charge is given to such a cluster, the charge will distribute itself along the peripheral regions so as to produce zero field inside the cluster body. However, one can observe that the perimeter regions making up the inner boundaries of the invaginations are electrostatically shielded (like the inner surface of a hollow conducting sphere). The unshielded perimeter, t_u, available for the charge distribution is only that which make up outer boundaries of the outward-extending ends ('tips' or 'buds'). In general, $t_u \ll t$. Like t, we assume that t_u is also scaling, i.e., $t_u \sim r^{d_c}$ where d_c is a new charging exponent. Obviously $d_c \ll d_f$. For Euclidean shapes $d_c = d_f = d - 1$. In case of highly ramified structures, when the boundary dimension $d_f \rightarrow d$, we expect that $d_c \rightarrow 0$ for two-dimensional clusters and $d_c \rightarrow 1$ for three-dimensional clusters. The reason for this is that in the case where $d = 2$ the charge concentrated on the unshielded tips will be like a distribution of point charges in space, and in the $d = 3$ case it will be like a distribution of line charges. Therefore, in general one can write that as $d_f \rightarrow d$, $d_c \rightarrow d - 2$. After a brief digression in the following paragraph, we will determine the capacitance on the basis of the above facts.

A similar exponent, d_u, was introduced earlier by Coniglio and Stanley [14] to describe the surface sites of an arbitrary fractal which are unscreened against trapping or the escape of a projectile having a different fractal dimension d_p. They concluded that $d_u = (d_f - 1) + (d - d_f)/d_p$. Their argument was based upon Hentschel's [15] treatment of the growth of diffusion-limited aggregates (DLA). In DLA the deep invaginated perimeter sites are not accessible to the random walker and their penetration depth $l \sim r^{(d-d_f)/d_w}$ where d_w is the random-walk dimensionality. On a similar line of reasoning, one can define the electrostatic shielding distance l_c for fractal metal clusters also. This is the average distance from the outermost periphery up to which surface-charge distribution persists. It should be stressed that, though l_c is not the same as l, their asymptotic behaviour under the limit $d_f \rightarrow d$ must be similar. Therefore, it is expected that $l_c \sim r^{\alpha(d-d_f)}$, where α is a constant unique to electrostatic problems. Notwithstanding this, however, I obtain the scaling relation for capacitance using a different argument.

Consider a cluster subjected to a small electric field, E. Charge polarisation will occur until an internal field E_{in} is set up that exactly balances the applied field, i.e., $|E| = |E_{in}|$. The induced dipole moment is therefore $P = Qr$, where Q is the polarised charge. If K be the polarisability of the cluster, then alternatively $P = KE = KE_{in}$. From elementary electrostatics we know that $E_{in} \sim \rho/r^{3-d}$ where ρ is the average polarised surface-charge density of one type (either positive or negative). One can write $\rho \simeq Q/t_u \sim Q/r^{d_c}$. Therefore,

$$E_{\text{in}} \sim Q/r^{3-d+d_c}. \tag{2}$$

Equating the two expressions for P and using (2) we conclude that

$$K \sim r^{4-d+d_c}. \tag{3}$$

For Euclidean clusters, $d_c = d - 1$ and $K \sim r^3$, a well known result in electrostatics. To find the capacitance we can alternatively write $E_{\text{in}} = V/r$, where V is the potential difference across opposite faces of the polarised cluster. Again, from $Qr = KE_{\text{in}} \sim r^{4-d+d_c}V/r$ we obtain, for the cluster capacitance $C = Q/V$,

$$C \sim r^{2-d+d_c}. \tag{4}$$

Therefore, the scaling relation for the charging energy becomes

$$E_c \sim r^{d-2-d_c}. \tag{5}$$

One can see that for Euclidean objects ($d_c = d - 1$) the capacitance exponent becomes unity in all dimensions.

Next we consider the hopping transport. It is agreed that the basic charge-transport mechanism is the same as the well known Mott variable-range-hopping between localised states in amorphous solids [16]. Ambegaokar and co-workers [17] and Pollak [18] have developed its general theory by employing the concept of the critical percolation path. In order to apply this theory to the charge transport across a metal cluster system of discontinuous films, it is important to identify clearly the quantities analogous to the localised states, their energy and tunnelling distances. A localised state in an amorphous solid is characterised by an exponentially decaying wavefunction with a decay constant α. The spatial separations between them is much larger than the localisation length. For tunnelling purposes they are point states, and the tunnelling distances are 'centre to centre' separations between them. In case of metal clusters, the localisation length of a carrier is of the order of the cluster size, and tunnelling can occur only between the unshielded tips of the clusters. Thus the tunnelling distances are the narrowest intertip separations. The wavefunction decay in the tunnelling regions (i.e. between two unshielded tips) is still characterised by an exponent decay constant α. The change in energy of a carrier in tunnelling from a cluster i to cluster j is essentially the difference in their charging energies $(E_{cj} - E_{ci})$. That is the analogue of localised state energies are the charging energies of the clusters. With this analogy in view the tunnelling conductance between a pair of clusters is given by [19]

$$G_{ij} = (\gamma_0 e^2/kT) \exp[-2\alpha R_{ij} - (|E_i| + |E_j| + |E_i - E_j|)/2kT] \tag{6}$$

where R_{ij} is the closest separation between unshielded tips; E_i, E_j are charging energies of clusters as given by (5); e is the electronic charge; k is Boltzman's constant; and γ_0 is a constant. Thus the conductance bonds between the clusters will be established via the narrowest tunnelling regions, and the critical percolation path characterised by the limiting conductance G_c will be established in a manner similar to that described in detail by Ambegaokar and co-workers [19] and Pollak [18]. The relevant density of states is now the density of the charging states, $D(E_c)$ (per unit volume per unit energy). $D(E_c)$ will be obtained from the cluster size distribution and (5) as follows.

Voss and co-workers [1] have demonstrated experimentally that the cluster-size distribution is compatible with the one given by percolation theory [17] and by Korcak–Mandelbrot law [20]. Percolation theory gives the average number of s-clusters (i.e. clusters consisting of s-sites) per lattice site $n_s \sim s^{-\tau}$, where the exponent τ obeys the

hyperscaling relation $\tau - 1 = d/d_f$. The spatial number density of the s-clusters will obviously be proportional to n_s. Recalling the scaling relations $s \sim r^{d_f}$ and $E_c \simeq r^{-c}$ with $c = 2 - d + d_c$, one can obtain

$$D(E_c) \propto n_s (\mathrm{d}s/\mathrm{d}r)(\mathrm{d}r/\mathrm{d}E_c) \sim E_c^{d/c-1}. \tag{7}$$

I stress that while calculating $D(E_c)$ one should use n_s instead of $p_s = sn_s$. The latter gives the probability that a given site, say the origin, belongs to an s-cluster. p_s measures the fractional space covered by s-clusters, whereas the quantity which matters in hopping conduction is their number density.

Since charging energies are independent of the sign of the charge, the Fermi level therefore lies midway between the positively and negatively charged states [9]. For $kT \ll E_c$ the probability of a cluster being charged is given by the Boltzmann factor $\exp(-E_c/kT)$. Hence a given cluster can remain positively or negatively charged with equal probability, and the tunnelling probability from this cluster to a neighbouring neutral one will also be equal for either of its charge states. This means that on one side of the Fermi level hopping occurs from positively charged clusters to neutral clusters, and on the other side from negatively charged clusters to neutral ones in a statistically symmetric manner. The density of states on either side of the Fermi level will be given by (7). Under a small external field, i.e. $e\Delta V \ll E_c$, where ΔV is the potential drop between clusters, the current contributions from both the hopping processes will add. Pollak [18] and Hamilton [21] have shown that, for density of states of the form $D(E) \sim |E|^n$, the temperature exponent of macroscopic conductivity is given by $x = (n + 1)/(n + d + 1)$. Therefore, using $n = d/c - 1$ from (7), we immediately arrive at

$$x = 1/(1 + c). \tag{8}$$

In effect, the dimension d in the variable-range-hopping formula with constant density of states in amorphous solids ($x = 1/(1 + d)$) [16, 18, 19] is replaced by the charging exponent $c = 2 - d + d_c$.

Near the percolation threshold, the cluster boundaries are highly ramified and $d_f \to d$. In such conditions, as argued earlier, $d_c \to d - 2$, therefore $c \to 0$, and $x \simeq 1$. On the other hand, away from the threshold in the non-scaling regime, the cluster shapes are nearly Euclidean and $d_c = d_f \to d - 1$. Therefore $c \to 1$, and $x \simeq 1/2$. For any intermediate situation $0 < c < 1$, therefore, $\frac{1}{2} < x < 1$. This provides a general explanation for the range of values assumed by the temperature exponent x in different films.

It is interesting to note that in cermets the metal grains are nearly Euclidean, therefore the conclusion $x = \frac{1}{2}$ above can also provide an explanation for their conductivity behaviour. However, recall that (8) was derived by assuming a power-law distribution of grain sizes. This distribution is of course verified for clusters of discontinuous films, but the grain-size distribution in cermets is reported to be log-normal [22]. I suggest that the present conclusion can still be valid, for the following reason.

Since the tunnelling occurs only from charged to neutral grains and the probability of smaller grains being charged is negligibly small due to the $\exp(-E_c/kT)$ dependence, conduction will therefore occur mainly via hopping among larger grains lying in the upper tail of the log-normal distribution. In this region the size distribution

$$f(r) = (2\pi\sigma^2)^{-1/2}(1/r) \exp[-(\ln r - \ln r_0)^2/2\sigma^2] \tag{9}$$

can be approximated as a power law

$$f(r) \simeq r^{-(1-\ln r_0/2\sigma^2)} \tag{10}$$

for $\ln r_0 < \ln r \ll 2\sigma^2$, where the various terms have their usual meaning. This is so

because $(\ln r - \ln r_0)^2 = (\ln r)^2 - 2 \ln r \ln r_0 + (\ln r_0)^2$, $\exp[-(\ln r)^2/2\sigma^2] = r^{-(\ln r)/2\sigma^2}$ and $\exp[(2 \ln r \ln r_0)/2\sigma^2] = r^{2\ln r_0/2\sigma^2}$. Using these in (9), one obtains

$$f(r) = (2\pi\sigma^2)^{-1/2} \exp[-(\ln r_0)^2/2\sigma^2] r^{-(1-\ln r_0/2\sigma^2)-(\ln r - \ln r_0)/2\sigma^2}.$$

Under the condition that $\ln r > \ln r_0$ and $(1 - \ln r_0/2\sigma^2) \gg (\ln r - \ln r_0)/2\sigma^2$ one obtains (10).

In brief, it is argued that the scaling relation usually assumed for the electrostatic charging energy of metal grains $E_c \sim 1/r$ will be in error if the grain shapes are irregular. For fractal grains a large fraction of the surface is electrostatically shielded. Assuming that the unshielded surface area t_u is characterised by a new exponent d_c as $t_u \sim r^{d_c}$, we obtain $E_c \sim 1/r^c$ where $c = 2 - d + d_c$, and $0 < c < 1$. Taking this into account, and using the cluster size distribution $n_s \sim s^{-\tau}$ given by percolation theory, it is shown that the fractional temperature exponent of the low-field DC conductivity of discontinuous films becomes $x = 1/(1 + c)$, i.e., $\frac{1}{2} < x < 1$. This explains the observed values of x. Also, the possibility of explaining cermet conductivities as well, which show $x = \frac{1}{2}$, is suggested.

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