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Conduction in granular metals—the effect of the grain separation distribution

Andrzej Kolek

Department of Electrical Engineering, Technical University of Rzeszów, Wincentego Pola 2, 35-959 Rzeszów, Poland

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Abstract. A charging energy model of conduction in granular metals has been considered. It has been shown that the temperature dependence of the DC conductivity, $\sigma \sim \exp[-(T_1/T)^{1/2}]$, interpreted as a crossover between high- and low-temperature behaviour can in fact be explained as resulting from flat parts of both the density of states and the distribution of tunnelling distances. It has also been shown that such distributions can appear in real metal–insulator composites. Models of hopping conduction in regular lattices and in continuous systems of hard and soft grains have been proposed. A comparison with experiments has been given as well.

1. Introduction

Granular metals are metal–insulator composites formed from small nanometre sized interdispersed metal and insulator grains. They are usually produced as films grown by co-evaporation or co-sputtering. Depending on the metal volume fraction ϕ there are two regions of electronic conduction in granular metals. When the concentration of metal is small, metal grains form isolated islands embedded in an insulating matrix. This region is called the dielectric region. As the metal volume fraction increases, islands form an infinite metallic cluster which spans the whole sample. This is the metal–insulator transition to the metallic region where the temperature coefficient of resistance is positive. In this region the DC conductivity, σ , fits the percolation power law (Kirkpatrick 1973) $\sigma \sim (\phi - \phi_c)^t$.

Values for the percolation threshold ϕ_c lie within the range 0.16–0.6 (Deutscher *et al* 1983). The lower part of this interval corresponds to the so-called random composites, whereas the upper part is typical for granular materials (Abeles *et al* 1975a, McAlister *et al* 1985). Thus in most cases ϕ_c exceeds the Scher–Zallen (1970) invariant of 0.16. This is explained in terms of dimensionality effects, namely a crossover from 3D to 2D behaviour (McAlister *et al* 1985, Gadenne and Gadenne 1989), correlation effects (preferential nucleation in metal grains) (Cohen *et al* 1978) and segregation effects (Balberg and Binenbaum 1987a) (random close packing predicts $\phi_c = 0.64$). Values for the exponent t have been found to vary between 1 and 2 (Abeles *et al* 1975a, Deutscher and Rappaport 1979, Deutscher *et al* 1983, McAlister *et al* 1985, Balberg *et al* 1990), in good agreement with percolation theory predictions for 2D and 3D (see e.g. Stauffer 1985, Kolek and Kusy 1988).

In the dielectric regime, electrical conduction is by electron hopping between metallic grains. In this process charge carriers are transported from one grain to another via thermally activated tunnelling. The temperature dependence of conductivity in this region has been widely observed to behave as

$$\sigma \sim \exp[-(T_1/T)^{1/2}] \quad (1)$$

(Sheng *et al* 1973, Abeles *et al* 1975a,b, Chui *et al* 1981, McAlister *et al* 1984, 1985, Gilabert *et al* 1989). A similar temperature dependence has also been observed for heavily doped semiconductors. It is commonly argued that, in semiconductors, equation (1) originates from variable-range hopping in the Coulomb gap (Efros and Shklovskii 1975, Shklovskii and Efros 1984). This approach has also been extended to granular metals (Chui *et al* 1981, Entin-Wohlman *et al* 1983, Chui 1991). Another approach interprets equation (1) as a crossover from high-temperature Arrhenius behaviour $\sigma \sim \exp(-E_H/T)$ to the low-temperature behaviour of Mott's variable-range hopping law $\sigma \sim \exp[-(T_0/T)^{1/4}]$ (Sheng and Klafter 1983, Klafter and Sheng 1984, Chen *et al* 1990, Zhou *et al* 1992, Sheng 1992). Both approaches have been criticized in a number of papers by Adkins (1982, 1987, 1989).

This paper deals with the second approach, with the aim to point out the importance of the distribution of intergrain separations. We show, in particular, that dependence (1) results in fact from a flat or nearly flat distribution of intergrain separations. The rest of the paper is organized as follows. In section 2 we detail a model to be considered. In section 3 we analyse this model using a critical path method. Section 4 contains a discussion on the range of validity of equation (1). The question of how this range is influenced by a distribution of tunnelling distances is also answered. As a result two models for hopping conduction in systems of penetrable and impenetrable spheres are proposed in section 5 and 6. Finally in section 7 we provide comments on the criticism of the model given by Adkins (1982, 1987) and summarize our findings.

2. Model

The most recent description of the model we are going to deal with was given by Zhou *et al* (1992). In this model conductance G_{ij} between grains i and j is expressed as the product of the probabilities for thermal activation and tunnelling (Miller and Abrahams 1960)

$$G_{ij} = G_0 \exp(-2\chi s_{ij} - E_{ij}/kT) \quad (2)$$

where χ is the decay rate of the electron wave function in the insulator, s_{ij} is the distance between two grains, k is Boltzmann's constant, T is absolute temperature and E_{ij} is the activation energy given by $E_{ij} = \frac{1}{2}(|E_i| + |E_j| + |E_i - E_j|)$. Here E_i denotes the grain's energy level. For each grain i energy E_i is the sum of two components: the grain's charging energy E_c and the energy in a random potential field (Adkins 1987, Chen *et al* 1990, Zhou *et al* 1992, Sheng 1992). The grain's charging energy is the energy required to place a charge on a neutral grain. For a spherical particle of diameter D its capacitance $C = \epsilon D/2$ and the charging energy $E_c = e^2/2C = e^2/\epsilon D$. Here ϵ is the effective dielectric constant of granular material, which can be different from that of an insulator (Abeles *et al* 1975b, Sheng and Klafter 1983). Since the charging energy is inversely proportional to grain diameter, a distribution of grain sizes leads to a distribution of charging energies. Thus we have (Adkins 1982, 1987, Chen *et al* 1990, Zhou *et al* 1992, Sheng 1992)

$$N(E_c) = (1/\sqrt{2\pi}\mu E_c) \exp[-\ln^2(E_c/E_0)/2\mu^2] \quad (3)$$

because a log-normal distribution of grain sizes has been observed in real mixtures (see e.g. Granqvist and Buhrman 1976, Romanowski and Kępiński 1980, Grannan *et al* 1981). Above E_0 and μ are the median value and standard deviation of E_c . They correspond to the median and standard deviation of the grain size distribution. Measurements show that μ lies in the range from 0.2 to 0.5.

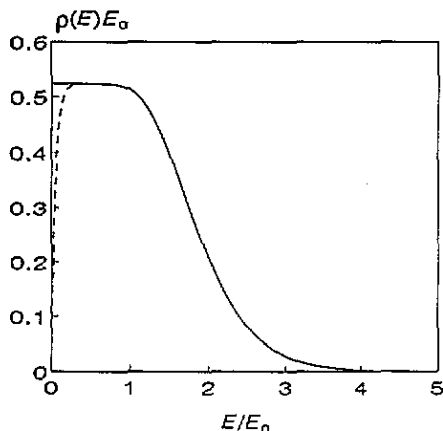


Figure 1. The density of grain energy levels, as in equation (4), which includes both the effects of charging energy and the disordered potential. E_0 is the median energy. The standard deviation μ for which the plot is drawn is 0.3. A dip in the density of states, marked by a broken curve, appears when a smooth function, rounding off the discontinuities of the distribution of the random potential at $\pm E_c$ is used in equation (4).

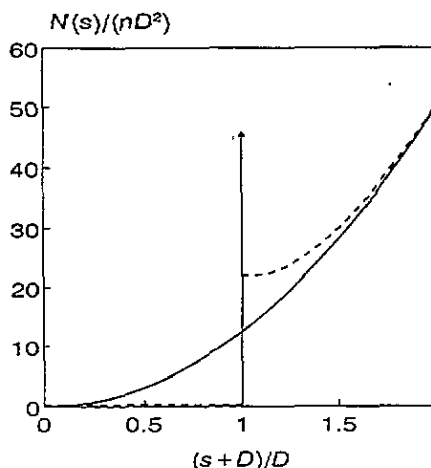


Figure 2. The distribution of separations between the central grain, which is taken to be at the origin, and the centres of the remaining grains in a system of penetrable spheres (full curve) and impenetrable spheres (broken curve). D is the sphere diameter and n is the number density. In the case of penetrable grains $N(s) = 4\pi(D + s)^2 n$. For impenetrable spheres $N(s) = 0$ for $s < D$. The delta function represents spheres which exactly touch the central grain.

The presence of a large disordered potential in granular metals has been observed experimentally in a number of field-effect measurements on discontinuous metal films (Adkins *et al* 1984, Adkins 1990). This random potential can locally shift the grain's energy E_c . This shift however cannot be greater than $\pm E_c$ since, otherwise, the grain can change its charge state (autoionize) and move closer to the Fermi level. Thus if we assume that the distribution of random potential $f(E)$ is uniform within $\pm E_c$, i.e. $f(E) = \frac{1}{2} E_c$ for $|E| < E_c$ and $f(E) = 0$ otherwise, we can calculate the spectrum of charging energies modified by a random potential (Adkins 1987, Chen *et al* 1990, Zhou *et al* 1992, Sheng 1992)

$$\rho(E) = \int_0^\infty N(E_c) f(E - E_c) dE_c = \frac{e^{\mu^2/2}}{2E_0\sqrt{\pi}} \int_{\mu/\sqrt{2} + \ln(E/2E_0)/\mu\sqrt{2}}^\infty e^{-y^2} dy. \quad (4)$$

If a smoother function $f(E)$ is chosen in equation (4), in order to temper discontinuities in the distribution of the random potential at $\pm E_c$ a small dip at $E = 0$ appears in $\rho(E)$, as is shown in figure 1 (Zhou *et al* 1992, Sheng 1992). This is in agreement with what has been observed in tunnelling experiments (Abeles *et al* 1975b). This explanation of a gap existing in the density of states at the Fermi level differs reasonably from that of Entin-Wohlman *et al* (1983) who found the origin of the gap as a typical Efros-Shklovskii (1975) correlation Coulomb gap. It is seen in figure 1 that the spectrum of grain energies has a flat part near $E = 0$. For such a defined model it was shown by the number of numerical calculations that the overall DC conductivity, σ , follows the law $-\ln \sigma \sim T^{-1/2}$ over several orders of magnitude in conductance and over more than a decade in temperature (Chen *et al* 1990, Zhou *et al* 1992, Sheng 1992). The observed relation has been explained as a crossover between high- and low-temperature behaviours.

To my knowledge no analytical derivation of equation (1), in terms of the model described above, has been given. It has even been stated that equation (1) does not arise as a characteristic dependence (McAlister *et al* 1984), so at the moment the question of why the value of $\frac{1}{2}$ fits this crossover in the best way seems unanswerable.

The basic idea of the above model is the concept of charging energy. The large effect of this energy on the conduction in granular metals was first considered by Neugebauer and Webb (1962) and next by Sheng *et al* (1973) and Abeles *et al* (1975b) who were able to explain the $-\ln \sigma \sim T^{-1/2}$ dependence, however they assumed correlations between grain sizes and intergrain separations. Because no such correlations have been observed (Šimanek 1981, Morris *et al* 1990) Sheng and Klafter (1983) and Klafter and Sheng (1984) rejected grain size/separation correlations but argued that the dependence $-\ln \sigma \sim T^{-1/2}$ results from interpolation between high- and low-temperature behaviour, as we have mentioned above.

3. Critical path analysis

In this section we apply the critical path method (Ambegaokar *et al* 1971) to the model described above. It was shown by numerical calculations on regular (Berman *et al* 1986) and random (Priolo *et al* 1992) networks that if intersite conductances G_{ij} are widely distributed, the overall conductance of the network is determined by the so-called critical conductance G_c i.e. $\sigma \sim G_c$. The latter is described as the largest value for G_{ij} which can be removed from a network without cutting it off. In other words, the subset of bonds with $G_{ij} > G_c$ forms a network which is at the percolation threshold, the so-called critical network. It is well known, however, that the critical network should contain on average B_c bonds per site. In the case of a d -dimensional discrete lattice, $B_c = p_c z$ where p_c and z are the bond percolation threshold and lattice coordination number, respectively, and B_c was shown to be approximately invariant, $B_c \simeq d/(d-1)$ (see e.g. Kirkpatrick 1973, Shklovskii and Efros 1984). The find G_c note that the bonds which form the critical network should satisfy the bonding criterion, $G_{ij} > G_c$ which can also be rewritten in the form (Ambegaokar *et al* 1971, Sheng and Klafter 1983)

$$s_{ij}/s_m + \frac{1}{2}(|E_i| + |E_j| + |E_i - E_j|)/E_m \leq 1 \quad (5)$$

where $s_m = \ln(G_0/G_c)/2\chi$ and $E_m = \ln(G_0/G_c)kT$ are the maximum allowed tunnelling distance and the maximum allowed energy of the grain. Thus to form the critical network it is required (Sheng and Klafter 1983, Halpern 1987) that

$$\int_{-E_m}^{E_m} dE_i \rho(E_i) \int_{-E_m}^{E_m} dE_j \rho(E_j) \int_0^{\max s_{ij}} ds_{ij} N(s_{ij}) / \int_{-E_m}^{E_m} dE_i \rho(E_i) = B_c \quad (6)$$

where $N(s_{ij})$ is a distribution of tunnelling distances and $\max s_{ij}$ is the maximum distance which satisfies condition (5) for a given set of E_i and E_j . Now we apply a critical path method to the model described in section 2. First let us solve equation (6) for the range of temperatures where both the distributions i.e. the density of states and the distribution of tunnelling distances, can be treated as constants. In this case we have $\rho = \rho(E \rightarrow 0) = e^{\mu^2/2}/2E_0$ and $N(s_{ij}) = N(s) = z/A$ if only hops to the nearest (z) neighbours are allowed and tunnelling distances are uniformly distributed on the lattice spacing A . In the case when n grains of diameter D are randomly dispersed in the unit

volume, the density of nearest neighbours is approximately $N(s) = 4\pi D^2 n$, which is a good approximation as long as the distance s is small compared with the grain diameter D . Thus we have

$$B_c = s_m E_m \rho z / 2A \quad \text{or} \quad B_c = s_m E_m 2\pi D^2 n.$$

These relations immediately lead to equation (1) with the characteristic temperature T_1

$$T_1 = 4A\chi B_c / z\rho k \quad \text{or} \quad T_1 = \chi B_c / \pi D^2 n \rho k = B_c \chi D / 6\phi \rho k \quad (7)$$

for percolation on a lattice or on a random arrangement of grains, respectively. In the latter case we have replaced the number density n by the metal volume fraction $\phi = n\pi D^3/6$. The results obtained are in good agreement with numerical calculations of hopping on a regular lattice (Chen *et al* 1990), as well as on a random set of grains (Sheng and Klafter 1983).

Now let us turn to the low-temperature limit. In this region the low-energy part of the density of states $\rho(E)$ is probed (to minimize the E_{ij}/kT term of G_{ij}), so a constant density of states approximation remains valid once more. Simultaneously longer hops are allowed (of order E_{ij}/kT) and the approximation of a constant density of tunnelling distances no longer holds. In the case when only nearest-neighbour hops on the lattice are allowed $N(s)$ vanishes for $s > A$. In the case of a random arrangement of grains, longer hops are possible and $N(s) = 4\pi(D+s)^2 n \simeq 4\pi s^2 n$ for $s \gg D$. The last approximation is however restricted to a very small metal volume fraction ϕ , where interactions between grains and screening effects can be neglected. The critical path method applied in this case yields

$$B_c = (z\rho E_m/2)(3 - 3A/s_m + A^2/s_m^2) \quad (8)$$

or (Ambegaokar *et al* 1971, Sheng and Klafter 1983)

$$B_c = \text{constant} \times n\rho s_m^3 E_m \quad (9)$$

for nearest-neighbour hopping on a discrete lattice or on a random set of grains in the limit $\phi \rightarrow 0$, respectively. Equation (8) leads to Arrhenius-type behaviour

$$\sigma \sim G_c \simeq G_0 \exp(-2A\chi) \exp(-E_L/kT) \quad (10)$$

with activation energy

$$E_L \simeq 2B_c/3\rho z. \quad (11)$$

We can view the above result more qualitatively. For low temperatures, E_{ij}/kT becomes a limiting term in G_{ij} . Since E_{ij} are strongly correlated (E_{ij} and E_{jk} are correlated through E_j) percolation occurs *through sites* with minimal energy. The activation energy is the minimum energy required to reach the percolation threshold

$$\int_{-E_L}^{E_L} dE \rho(E) = x_c \quad (12)$$

where x_c denotes the site percolation threshold. Combining equations (11) and (12) we obtain

$$x_c = 4B_c/3z = \frac{4}{3} p_c$$

which can be found as an approximate relation between site and bond percolation thresholds.

In the case of a random arrangement of grains, equation (9) leads to the well known Mott behaviour $-\ln \sigma \sim T^{-1/4}$. Thus we have shown in a quantitative way that the model described in section 2 exhibits a low-temperature behaviour, qualitatively described in section 1. At this point we can state that this model serves as an explanation for experiments on granular metals, in which the temperature dependence of conductivity is well fitted by $-\ln \sigma \sim T^{-1/4}$ at very low temperatures and by the $-\ln \sigma \sim T^{-1/2}$ law as the temperature moves to higher values. Such a behaviour was observed, for example, in co-sputtered Au-SiO₂ films (McAlister *et al* 1984, 1985) and Pt-Al₂O₃ and Au-Al₂O₃ cermets (Gilabert *et al* 1989).

Finally let us consider the high-temperature limit. In this case thermal activation is easy and the tunnelling part of G_{ij} becomes a limiting factor. Short hops are preferred, so a constant distribution of tunnelling distances is a reasonable approximation. For sufficiently high temperatures we have $E_m \gg 2E_0$ and $\rho(E) \simeq 0$ and $\int \rho(E) dE = 1$ can be used in calculations of the average number of bonds per site

$$B_c = s_m(1 - 5E_0/6E_m)N(s) \quad (13)$$

where, as we discussed earlier, $N(s)$ takes z/A in the case of hopping on a regular lattice or $4\pi D^2 n$ when a random arrangement of grains is considered. As we expect, equation (13) yields a simple Arrhenius law

$$G_c = G_0 \exp(-2\chi B_c/N(s)) \exp(-E_H/kT). \quad (14)$$

with an activation energy $E_H = 5E_0/6$. We find this result correct because, at high temperatures, correlations among intergrain conductances G_{ij} are small. The conducting network is formed from bonds of lowest conductances (distances). Thus the activation energy should be equal to the average value for intergrain energies E_{ij} which indeed, in the case of a constant density of states, were found to be $5E_0/6$ (see e.g. Shklovskii and Efros 1984). Thus we have

$$E_H = \langle E_{ij} \rangle = \frac{5}{6} E_0.$$

Since the terms E_{ij}/kT at high temperatures are small, the conductivity, σ , is determined by the largest tunnelling distance, s_H , required to form a percolating network, which can be found from the appropriate percentile of the distribution of tunnelling distances

$$\int_0^{s_H} ds N(s) = N(s)s_H = B_c \quad (15)$$

which qualitatively explains the result obtained in equation (14).

4. Range of validity of $-\ln \sigma \sim T^{-1/2}$ law

Now let us comment on the temperature region in which the fractional dependence $-\ln \sigma \sim T^{-1/2}$ is valid. First, let us note that as the temperature is lowered, the conductivity σ decreases (see equations (14), (10), (1)). This means that the distance, s_{crit} , of the critical hop increases as the energy, E_{crit} , of the critical hop decreases due to T being lowered. In the temperature range where the relation $-\ln \sigma \sim T^{-1/2}$ holds, a competition between

tunnelling and activated terms of G_{ij} occurs, so that both components of the exponent in equation (2) are comparable to each other and vary with temperature in the same way

$$2\chi s_{\text{crit}} \simeq E_{\text{crit}}/kT \sim \sqrt{T_1/T}. \quad (16)$$

Thus the temperature range, where $-\ln \sigma \sim T^{-1/2}$ holds, corresponds to the range of distances s in which the critical distance, s_{crit} , can vary and in which the distribution $N(s)$ is approximately constant. The distance s_{crit} is limited both at low temperatures, $s_{\text{crit}} < s_L = A$, $s_{\text{crit}} < s_L \ll D$ and at high temperatures, $s_{\text{crit}} > s_H$ (see equations (14), (15)), so the region of validity of the $-\ln \sigma \sim T^{-1/2}$ relation seems to be narrow. For example, in the case of hopping on a simple cubic lattice we have $s_H = AB_c/z = Ap_c$, $s_L = A$, $s_L/s_H = 1/p_c \simeq 4$ which, according to equation (16), corresponds to $T_H/T_L = 16$, where T_H and T_L are the high- and low-temperature limits of the dependence $-\ln \sigma \sim T^{-1/2}$. Although most experimental data can be completely covered by such a temperature variation (Abeles *et al* 1975a, b, Sheng *et al* 1973, McAlister *et al* 1984) there are some which exhibit a $-\ln \sigma \sim T^{-1/2}$ dependence over the range $T_H/T_L \simeq 200$ (Chui *et al* 1981). In our opinion this is the main reason for the criticism of the nearest-neighbour model of hopping conduction in granular metals. However, we should notice that the ratio of the limits of critical hops

$$s_L/s_H = 1/p_c = z/B_c$$

can easily be increased if further hops, for example to second-nearest neighbour or third-nearest neighbour, are allowed. This has an effect of increasing the lattice coordination number, z , reducing the value for the percolating threshold and, as a result, increasing the ratio s_L/s_H . For example, if on a simple cubic lattice hops up to the third-nearest neighbour are possible, then $z = 26$ and $s_L/s_H \simeq 17$, which is sufficient enough to support the dependence $-\ln \sigma \sim T^{-1/2}$ over $T_H/T_L = 17^2 = 289$, which is greater than the reported value $T_H/T_L \simeq 200$. In granular metals there are, however, other effects which can lead to an increase of the ratio s_L/s_H . The first is that some grains touch each other, so to form a percolating cluster much smaller number of tunnelling bonds is necessary. This lowers the value for s_H and the ratio s_L/s_H increases. This effect is especially important near the metal-insulator transition, where the size of the metallic clusters and thus the number of metallic connections is large. Another effect is the change of the radii distribution function. The number of grains lying a distance s from a given central particle equals $N(s) = 4\pi(D+s)^2n$ only in the case of non-interacting, fully penetrable, grains. For interacting, impenetrable, hard grains $N(s)$ is modified in a way shown schematically in figure 2. This effect is again more and more significant as the metal volume fraction increases. Finally let us note that screening of further grains by the nearest neighbours also leads to a flattening of $N(s)$. All the effects mentioned above make the assumption of a constant distribution of tunnelling distances quite reasonable. Interestingly, according to what we have just said, the temperature range in which the law $-\ln \sigma \sim T^{-1/2}$ holds should be smaller for cermets, which are deep in the dielectric regime, and it should increase as the metal-insulator transition is approached. Such a rule could be observed when analysing experimental data. The ratio $s_L/s_H = (T_H/T_L)^{1/2}$ deduced from plots of $-\ln \sigma \sim T^{-1/2}$ increases from approximately 1.25 for $\phi = 0.04$ or 1.7 for $\phi = 0.08$ (Abeles *et al* 1975b) to 3.5 for $\phi = 0.4$ (Abeles *et al* 1975a) or even to 14 for the samples which are very close to the metal-insulator transition ϕ_c (Chui *et al* 1981). In the following sections we will try to incorporate some of the effects already mentioned in a more quantitative way for the systems of interacting and non-interacting spherical particles.

5. Hopping conduction in a system of penetrable grains

The system of fully penetrable spherical grains has been found as a very realistic model of metal-insulator composites (see e.g. Feng *et al* 1987 for a review). The model was called an 'inverted random void model' and it was extensively studied above the percolation threshold, which was found at $\phi_c \simeq 0.3$ (see e.g. Balberg and Binenbaum 1987a, b, Shklovskii and Effros 1984). The system consists of spherical grains of diameter D with centres randomly (Poisson) distributed in 3D space. Since grains can overlap, the volume fraction of the metallic (grain) phase relates to the excluded volume through (see e.g. Shklovskii and Efron 1984)

$$\phi = 1 - \exp(-(\pi D^3/6)n)$$

where n is the concentration of grain centres (the number density). The average number of grains which overlap a given grain, i.e. the number of metallic bonds per grain (site) B , is given by the number of centres included in a sphere of radius D

$$B = \frac{4}{3}\pi D^3 n.$$

The volume fraction of metal ϕ can thus be also expressed as

$$\phi = 1 - \exp(-B/8).$$

Below the percolation threshold, for $\phi < \phi_c$, B is too small to form a percolation cluster. To form such a cluster B is required to equal $B_c = -8 \ln(1 - \phi_c) \simeq 2.8$ (Shklovskii and Effros 1984, Balberg and Binenbaum 1987b) bonds per site. Thus metallic bonds should be completed by the number of tunnelling connections to reach B_c

$$B_c = B + \int_{-E_m}^{E_m} dE_i \rho(E_i) \int_{-E_m}^{E_m} dE_j \rho(E_j) \int_0^{\max_{s_{ij}}} ds_{ij} N(s_{ij}) / \int_{-E_m}^{E_m} dE_i \rho(E_i).$$

Following the analysis of section 3 with a constant density of states ρ , and a uniform distribution of tunnelling distances $N(s) = 4\pi D^2 n = -24 \ln(1 - \phi)/D$, we again obtain the fractional dependence of equation (1), with

$$T_1 = 4\chi D \ln[(1 - \phi_c)/(1 - \phi)] / 3\rho k \ln(1 - \phi). \quad (17)$$

As we have already discussed in section 4 the range of validity of $-\ln \sigma \sim T^{-1/2}$ is rather wide, especially near ϕ_c . In this case the difference $B - B_c$, which should be put in the RHS of equation (15) to determine s_H , the high-temperature limit of tunnelling distances, tends to zero, and s_L/s_H increases significantly. We can rewrite equation (17) in the form which takes into account relations between ρ , E_0 and D , $\rho \simeq \frac{1}{2}E_0$, $E_0 = e^2/\epsilon D$

$$T_1 = \eta \{8 \ln[(1 - \phi_c)/(1 - \phi)] / 3k \ln(1 - \phi)\} \quad (18)$$

where $\eta = e^2 \chi / \epsilon$. To test our result we fitted some of the experimental data to equation (18), as is shown in figure 3. The value $\eta = 0.23$ eV, for which equation (18) is drawn in figure 3, is only an order of magnitude smaller than the expected value $\eta = 3.8$ eV. This discrepancy, however, can be understood if we note that the permittivity of an insulator, which was used to calculate the value 3.8 eV, can differ from that of granular metal (Abeles *et al* 1975b, Sheng and Klafter 1983). In fact, ϵ is ϕ dependent, which can additionally modify the dependence of T_1 versus ϕ in figure 3. As we can see in figure 3, there are also data that cannot be fitted by equation (18) because they exhibit a much greater value for the percolation threshold than $\phi_c \simeq 0.3$. In this case a model of impenetrable grains seems to be more adequate. (The immediate advantage is that it exhibits $\phi_c = 0.64$ (see Balberg and Binenbaum 1987a, b).)

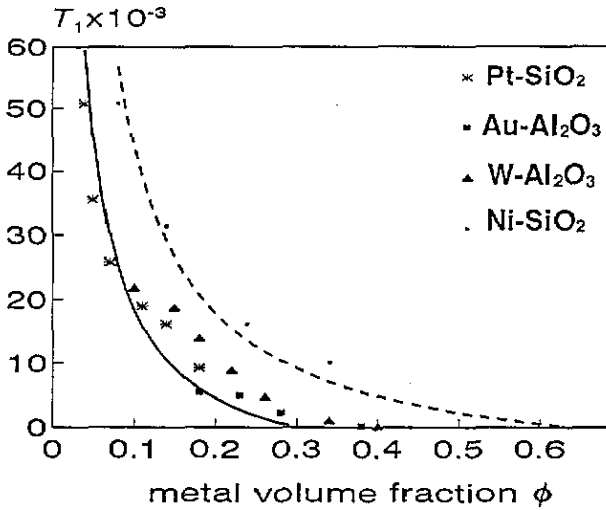


Figure 3. The temperature T_1 , which acts in the dependence $-\ln \sigma \sim (T_1/T)^{1/2}$. Curves are drawn according to equations (18) (full) and (20) (broken) which are derived for hopping conduction models of penetrable and impenetrable grains, respectively. The points refer to experiments reported by Abeles *et al* (1975a, b).

6. Hopping in a system of hard grains

In a system of spherical particles which cannot overlap, the critical volume fraction rises to $\phi_c \simeq 0.64$ (see e.g. Balberg and Binenbaum 1987a, b) which is the random close packing limit. It has also been shown that at percolation the average number of bonds (the number of touching grains) per grain drops to about 1.5 (Balberg and Binenbaum 1987b). Thus $B_c = 1.5$ should be used instead of 2.8 in further calculations. By analogy to lattice percolation we can relate linearly the average number of bonds per grain, B , with the grains' (metal) volume fraction ϕ . For $\phi < \phi_c$ there is also $B < B_c$ and the number of tunnelling bonds required to reach the percolation threshold is

$$B_c - B = B_c(1 - \phi/\phi_c) = \int_{-E_m}^{E_m} dE_i \rho(E_i) \int_{-E_m}^{E_m} dE_j \rho(E_j) \times \int_0^{\max s_{ij}} ds_{ij} N(s_{ij}) / \int_{-E_m}^{E_m} dE_i \rho(E_i). \tag{19}$$

In a system of impenetrable spheres the distribution of tunnelling distances is changed in the way shown in figure 2. Since we do not know the exact form of $N(s)$, only approximate calculations are possible. If we neglect the effect of the changed form of $N(s)$ for $s > D$ and solve equation (19) for $N(s) = 4\pi D^2 n = 24\phi/D$, i.e. for the lower bound of $N(s)$, we obtain equation (1) with temperature T_1

$$T_1 = (B_c/3k)(1/\phi - 1/\phi_c)\eta. \tag{20}$$

In figure 3 we plot equation (20), trying to fit the data with larger values for ϕ_c . The parameter $\eta = 0.9$ which we used is quite reasonable if we realize that in fact the lower bound of $N(s)$ has been used to obtain equation (20), and all the comments on the effective

permittivity made in section 5 remain valid for the system of hard grains. A further study using the exact form of $N(s)$ is certainly needed at this point. Granular metals show a more complicated morphology which probably can be treated as an intermediate case between hard (impenetrable) and soft (penetrable) core limits, and equations (18) and (20) should be treated in the same way when fitting experimental data.

7. Summary

The approach presented to explain the relation $-\ln \sigma \sim T^{-1/2}$ as hopping on sites with energies and separations uniformly distributed in energy and physical space has been proposed by Šimanek (1981). It was questioned because it could not account for the wide temperature range through which $-\ln \sigma \sim T^{-1/2}$ was observed (Pollak and Adkins 1992). The temperature range for which the model works well is restricted to $T_H/T_L = (s_L/s_H)^2 \simeq p_c^{-2}$, which is less than the values observed in experiment (Chui *et al* 1981). In sections 4 to 6 we have shown how this criticism can be avoided if we allow electron hops to further neighbours and if we consider the role of metallic connections in forming the percolating network. Another criticism of Šimanek's approach was that in order to derive the dependence $-\ln \sigma \sim T^{-1/2}$, he optimized independently tunnelling distances and activation energies, which is clearly not the case (Adkins 1990). In our derivation a path of conductances G_{ij} is optimized.

Within the last few years some doubt has appeared as to whether the law $-\ln \sigma \sim T^{-1/2}$ can be observed in the model defined in section 2 (Adkins 1982, 1987). In the model analysed by Adkins (1982, 1987) a log-normal distribution of tunnelling distances was assumed. For such a system a simple activation, i.e. a linear dependence of $\ln \sigma$ versus inverse temperature, has been found. To obtain the bulk conductivity, σ , the effective medium theory (Kirkpatrick 1971) has been used. Unfortunately this method works well only with uncorrelated bond percolation problems and thus does not incorporate an important correlation effect among neighbouring connections. The hopping problem is in fact a site-bond percolation which crosses over to a pure bond (uncorrelated) percolation at high temperatures and to a pure site (correlated) percolation at low temperatures. This crossover is very important because it results in increasing the ratio of limiting activation energies E_H/E_L . As we have shown in our analysis this ratio takes the value $E_H/E_L = (5E_0/6)/(2B_c/3\rho z) \simeq 2.5$ for hopping on a simple cubic lattice. The greater the ratio E_H/E_L , the wider the region of hopping with decreasing activation energy, where the law $-\ln \sigma \sim T^{-1/2}$ is observed. Indeed this was observed in a number of numerical simulations (Chen *et al* 1990, Zhou *et al* 1992, Sheng 1992). If correlations between bonds are neglected, the problem is simplified to a pure bond percolation and a distribution of the bond's conductances can be used to solve the task. The effective medium theory or the critical conductance approximation (Tyč and Halperin 1989, Le Doussal 1989) can be used in this case to find the bulk conductivity. Independent of the method used, limiting high- and low-temperature activation energies can be easily deduced. As $T \rightarrow \infty$, E_H takes $\langle E_{ij} \rangle$, the average value for the intergrain energies distribution. As $T \rightarrow 0$, a percolating network is formed from bonds with the lowest E_{ij} , so E_L can be found from the appropriate percentile of $P(E_{ij})$, the intergrain energy distribution

$$\alpha = \int_0^{E_L} dE_{ij} P(E_{ij}).$$

If the critical conductance approximation is used $\alpha = p_c$, whereas $\alpha \simeq 1/d$ when the effective medium theory is used (Adkins 1982)†. This is obviously incorrect because in fact this percolating network is formed from bonds connecting sites of smallest energy E_i . For $\alpha = 1/d$ and distributions $P(E_{ij})$ calculated from $N(E_c)$ (equation (3)) or $\rho(E)$ (equation (4)), used by Adkins (1982, 1987), we obtain $E_H/E_L \simeq 1.4$ in both cases. Thus the approach in which a hopping mechanism is simplified to bond percolation causes the region of conduction with decreasing activation energy to be strongly reduced. Instead of $-\ln \sigma \sim T^{-1/2}$, only a simple activation with energy E_L (because of the analysed region of temperatures) has been detected. Similarly, if we neglect interbond correlations and apply the critical conductance approximation to the system with a flat distribution of tunnelling distances and constant density of states (which is the subject of the current paper), we obtain $E_H = \frac{5}{6}E_0$ for $T \rightarrow \infty$, $E_L = E_0\sqrt{4p_c/3}$ for $T \rightarrow 0$ and, interestingly, $-\ln \sigma \sim T^{-2/3}$ in the transition regime. This dependence, however, will be difficult to observe because $E_H/E_L \simeq 1.4$ in this case as well.

Summarizing, the charging energy model of conduction in granular metals has been analysed. It has been shown that the $-\ln \sigma \sim T^{-1/2}$ dependence, observed as a crossover between high- and low-temperature behaviour, can be explained as resulting from flattened parts of both the density of states and the distribution of tunnelling distances. It has also been shown that such distributions can appear in metal-insulator composites. When purely metallic connections between metal grains are taken into account, the temperature range, in which the relation $-\ln \sigma \sim T^{-1/2}$ is valid, is as wide as that observed for granular metals. In this case models of hopping conduction in systems of hard and soft grains have been proposed. A comparison with experiment can show us that these models work properly as models of conduction in granular metals.

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† Discrepancies between results given by the effective medium theory and critical conductance approximation were also pointed out by Kirkpatrick (1971) and Bernasconi (1973).

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