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# Simulation of the temperature dependence of the DC conductivity in granular systems with the effective medium theory

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**Abstract.** The effective medium theory has been used to simulate the temperature dependence of the DC conductivity in granular systems. Various grain size, intergrain separation and charging energy distributions have been tested. Non-activated hopping type dependences are obtained. The conditions to be fulfilled to obtain the thermal variation experimentally observed in most granular metals and conducting polymers are discussed.

## 1. Introduction

As far as electronic transport properties are concerned, electronic conducting polymers often display striking similarities with granular metal films and cermets for small metal concentrations [1, 2]. To the isolated nanometre-sized metallic grains randomly dispersed in the insulating matrix correspond highly doped polaronic clusters embedded in less doped regions inside the electronic conducting polymer. The orders of magnitude of the charging energies, of the diameters of the conducting islands and of the mean distances separating the grains are similar. In both types of material, the conduction process can be described as a thermally activated intergrain hopping phenomenon of the charge carriers. The DC conductivity,  $\sigma$ , is generally observed experimentally to behave as

$$\sigma(T) = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^\alpha\right) \quad (1)$$

with  $\alpha = 1/2$  in cermets and in many conducting polymers.

Many papers have been devoted to the calculation of the exponent  $\alpha$  (1). Nevertheless, the theoretical value of  $\alpha$ , and the relations between the various distances involved in the transport process, remain matters of controversy [3–9]. To ensure simply the homogeneity of the metallic grain concentration, Sheng *et al* have assumed the ratio,  $d/s$ , of the grain diameter,  $d$ , and of the thickness,  $s$ , of the insulating barrier which surrounds it, is a constant inside the material [3,4]. Some models do not require any relation between the island size and the grain separation but arrive at a fractional temperature dependence by evoking unphysical distributions of charging energies to place or remove one electron from a neutral grain [7, 8, 10]. With an approximate effective medium calculation, Adkins predicted that the conductivity should have an activated temperature dependence ( $\alpha = 1$ ) at all temperatures

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in the absence of any correlation between  $s$  and  $d$  [7, 8]. Sheng *et al* have also evaluated the conductivity with the optimal percolation path method, without any correlation between  $s$  and  $d$ , and assuming a finite density of state at the Fermi level due to impurities. They have obtained exponents  $\alpha$  between 1/4 and 1 [6].

The object of this paper is to take part in this discussion and to perform a complete numerical simulation of the temperature dependence of the conductivity based on the effective medium theory. We reexamine the values of the exponent  $\alpha$  obtained depending on

- (i) the correlation between the intergrain separation  $s$  and the grain size  $d$ ,
- (ii) the distributions of these distances and
- (iii) the presence of a disorder modifying the charging energy distribution.

We have also studied the effects related to the thermal variation of the various distribution widths, to be considered to account for the transport process. When the temperature changes, the sizes of the grains and the intergrain distances involved in the transport process are modified. The tunnelling distance between two localized states may depend on temperature because the charge carrier has to optimize the balance between tunnelling and activation.

Exponents higher than 1/2 but lower than 1 are obtained. The correlation between  $s$  and  $d$  is not necessary to ensure fractional exponents,  $\alpha < 1$ . We discuss the conditions to be fulfilled to obtain the value  $\alpha = 1/2$  which is the best to account for the experimental data.

In the first section, we describe the effective medium theory which serves as a basis for the numerical simulation and the parameters of our model. In the second section, we will describe and discuss the results.

## 2. The model

### 2.1. The effective medium theory

In the framework of the effective medium theory, the disordered material is replaced by a homogeneous effective medium. Each grain defines a site and two sites are linked together by a conductance determined by the transition rate between these two localized centres. Therefore, the system is described by a disordered resistor network with a distribution,  $f(\gamma)$ , of conductances between two nodes of the network. These random conductances are then replaced by a single average value,  $\gamma_{eff}$ , which is equal to the conductivity of the network and determined implicitly by the equation [11]

$$\int f(\gamma) \frac{\gamma - \gamma_{eff}}{\gamma + (d-1)\gamma_{eff}} d\gamma = 0 \quad (2a)$$

where  $d$  is the dimensionality of the medium.

The equation (2a) can be written, in a three-dimensional system,

$$3\gamma_{eff} \int \frac{f(\gamma) d\gamma}{\gamma + 2\gamma_{eff}} = 1. \quad (2b)$$

### 2.2. Transition rate

Following earlier work on disordered systems [12], we have assumed that the conductance or the transition rate connecting two metal grains  $i$  and  $j$  is determined by the charging

energies and the tunnelling process and given in the low-temperature limit by

$$\gamma_{ij} = \gamma_0 \exp\left(-2Ls_{ij} - \frac{E_{ij}}{kT}\right) \quad (3)$$

where  $s_{ij}$  denotes the distance between the grain surfaces along the line joining their centres,  $k$  is the Boltzman constant, and  $L$  is the decay rate of the electron wave function in the insulating region of the material. In the following, we have taken  $1 \text{ \AA}^{-1} < L < 3 \text{ \AA}^{-1}$ . Any larger variation of  $L$  will be included in the intergrain distance distribution.  $E_{ij}$  is the activation energy involved in the hopping process:

$$E_{ij} = \frac{1}{2}(|E_{c_i} - E_{c_j}| + E_{c_i} + E_{c_j}) \quad (4)$$

where  $E_{c_i} = e^2/\kappa C_i$  is the charging energy of the grain  $i$ ,  $\kappa$  is the effective dielectric constant of the granular metal and  $C_i$  the capacitance of the grain  $i$ .  $C_i$  is proportional to the diameter  $d_i$  of the grain  $i$ .

### 2.3. Intergrain distance, grain size and charging energy distributions

Realistic distributions of the size of the grains, of the charging energy and of the intergrain separations must be incorporated. In the case of granular metal films,  $d$  is expected to have a log-normal distribution as has been measured in detailed studies [13]:

$$P(d) = \frac{1}{\sqrt{2\pi}} \frac{1}{\mu_d} \frac{1}{d} \exp\left(-\frac{\ln^2(d/d_0)}{2\mu_d^2}\right) \quad (5a)$$

where  $\mu_d$  is the width of the distribution of  $\ln(d)$  and  $d_0$  the average grain size.

As the grain capacitance is inversely proportional to the grain size, in the absence of any disorder on the charging energies,  $E_c$  is described by a log-normal distribution:

$$P(E_c) = \frac{1}{\sqrt{2\pi}} \frac{1}{\mu_{E_c}} \frac{1}{E_c} \exp\left(-\frac{\ln^2(E_c/E_0)}{2\mu_{E_c}^2}\right). \quad (5b)$$

$E_0$  is the average charging energy and  $\mu_{E_c} = \mu_d$ . Detailed measurements of the size distribution show that  $\mu_d$  lies in the range 0.2–0.5 [3].

There has been little study of the distribution,  $Q(s)$ , of the intergrain separation distances  $s$ . Therefore, two distributions have been tested:

$$\begin{aligned} Q(s) &= \frac{1}{s_{max} - s_{min}} && \text{for } s_{min} < s < s_{max} \\ Q(s) &= 0 && \text{otherwise} \end{aligned} \quad (6a)$$

and

$$Q(s) = \frac{1}{\sqrt{2\pi}} \frac{1}{\mu_s} \frac{1}{s} \exp\left(-\frac{\ln^2(s/s_0)}{2\mu_s^2}\right). \quad (6b)$$

We have taken  $\mu_s$  in the range 0.2–0.5.

### 2.4. Charging energy disorder

A series of studies with discontinuous metal films have provided evidence for the presence in granular metals of large disorder potentials that can shift locally the energy of the grain away from the Fermi level of the system [7, 8]. An important source of disorder energy may be the variation in the work function associated with different crystallographic faces around the grains [14]. This shift cannot exceed  $\pm E_c$  since the ionization by one electronic

charge of the grain would then lead to a state closer to the Fermi level and it would be energetically favourable for the grain to change its charge state. To describe this ‘smearing effect’, we have used the smoothly varying function proposed by Zhou *et al* [5].

$$F(E) = N^{-1} \begin{cases} \tanh \left[ 10 \left( \frac{E_c + E}{E_c} \right) \right] & -E_c \leq E < 0 \\ \tanh \left[ 10 \left( \frac{E_c - E}{E_c} \right) \right] & 0 < E < E_c \\ 0 & \text{otherwise.} \end{cases} \quad (7)$$

Where  $N$  is a normalization constant. The new energy distribution function  $P^*$  is therefore the convolution of  $F(E)$  and  $P(E_c)$ :

$$P^*(E) = \int_0^\infty P(E_c) F(E - E_c). \quad (8)$$

### 2.5. Limits in the charging energies, grain sizes and intergrain distances involved in the transport process

At this point, we have to estimate the limits in the grain size, charging energy and intergrain distance distributions. These real limits in the distributions may influence the temperature dependence of the conductivity law [15].

The system cannot enclose infinitely large grains and the distribution of charging energy must satisfy the condition  $E_c > E_{c_{min}}$  where  $E_{c_{min}}$  is determined by the maximum diameter of the conducting grains.  $E_{c_{min}}$  has been estimated to be a few meV.

In the case of electronic conducting polymers, Zuppiroli *et al* derived the following expression for the charging energy [1]:  $E_c = 2Ua/d(1 + d/2s)$ . In this formula,  $U$  is the on-site Coulomb repulsion and  $a$  is the monomer size. With  $a \approx 5 \text{ \AA}$ ,  $U \approx 2 \text{ eV}$ ,  $d_{max} = 200 \text{ \AA}$ , and  $s_{min} = 1 \text{ \AA}$ ,  $E_{c_{min}}$  can be estimated to be 2 meV.

As far as the minimum intergrain barrier,  $s_{min}$ , is concerned, we have used  $s_{min} = 1 \text{ \AA}$ . The maximum intergrain distance  $s_{max}$  was estimated to be a few nanometres.

The maximum charging energy  $E_{c_{max}}$  is related to the minimum diameter of the conducting grains. The use of the transition rate  $\gamma_{ij}$  (3), requires a low electron–phonon coupling constant  $g$ . In the case of electronic conducting polymers, Zuppiroli *et al* have shown that  $g = 5/n$  where  $n$  is the number of monomers included in the conducting grain. The condition  $g \ll 1$  leads to a minimum grain size of the order of a few nanometres, and to maximum charging energies of a few hundred meV.

Alternatively to these values, independent of temperature, it is tempting, in order to evaluate the maximum charging energy,  $E_{c_{max}}$ , and the maximum intergrain barrier,  $s_{max}$ , involved in the transport process, to use some of the percolation theory results that suggest that these limits can depend on temperature. In the framework of the percolation theory, the system is conducting when the conductance  $\gamma_{ij}$  between the sites  $i$  and  $j$  is greater than a critical value  $\gamma_c$ . The conduction criterion  $\gamma_{ij} > \gamma_c$  can be expressed as

$$\frac{s_{ij}}{s_{max}} + \frac{E_{ij}}{E_{c_{max}}} \leq 1 \quad (9)$$

with

$$s_{max} = \frac{1}{2L} \ln \left( \frac{\gamma_0}{\gamma_c} \right) \quad (10)$$

$$E_{c_{max}} = kT \ln \left( \frac{\gamma_0}{\gamma_c} \right). \quad (11)$$

The critical conductance  $\gamma_c$  is also the conductance of the system and we can assume

$$\gamma_c \propto \exp\left(-\left(\frac{T_0}{T}\right)^\beta\right) \quad (12)$$

with  $1/4 \leq \beta \leq 1$ . We then obtain

$$s_{max} \propto \frac{1}{T^\beta} \quad (13)$$

and

$$E_{c_{max}} \propto T^{1-\beta} \quad (14)$$

where  $s_{max}$  and  $E_{c_{max}}$  are the maximum tunnelling distance and the maximum charging energy.

On the one hand, in the low temperature range, the activation process is difficult and the maximum tunnelling distance increases. Hopping is not restricted to the nearest-neighbour grains and to very small intergrain distances. On the other hand, in the high temperature range, the maximum charging energy and the number of charged grains contributing to the transport process increase. Activation is easier and nearest-neighbour hopping dominates the transport process. Therefore, depending on the temperature range, the number of grains involved in the hopping phenomenon changes and does not necessarily include the whole of the distribution.

In the calculations, for simplicity, the condition  $E_{ij} < E_{c_{max}}$  has been replaced by  $E_{c_i} < E_{c_{max}}$  and  $E_{c_j} < E_{c_{max}}$ .

At this point, (2b) can be written

$$3\gamma_{eff} \int \int \int_{\substack{E_{c_{min}} < E_{c_i} < E_{c_{max}} \\ E_{c_{min}} < E_{c_j} < E_{c_{max}} \\ s_{min} < s < s_{max}}} \frac{P(E_{c_i})P(E_{c_j})Q(s) dE_{c_i} dE_{c_j} ds}{\gamma + 2\gamma_{eff}} = 1. \quad (15)$$

### 3. Results and discussion

The numerical resolution of (10) has been undertaken with NAG library Fortran routines in the temperature range  $10 \text{ K} < T < 300 \text{ K}$ . We used among others the Patterson, Piessens and De Donker algorithms to estimate one-dimensional or multidimensional integrals and the Bus and Dekker algorithm devised to approximate the single roots of transcendental equations.

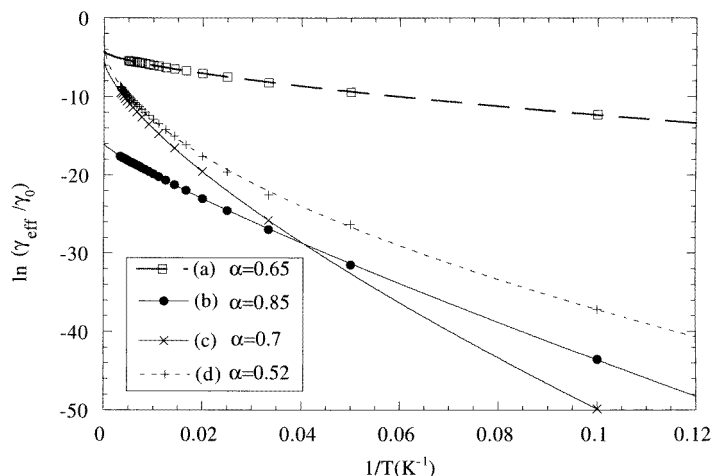
In figure 1 are displayed the variations of  $\ln(\gamma_{eff}/\gamma_0)$  versus  $1/T$  in four distinct typical cases which differ depending on whether

- (i)  $d$  and  $s$  are correlated,
- (ii) the distribution of charging energies is modified by random potentials and
- (iii) the maximum intergrain distance  $s_{max}$  and the maximum charging energy  $E_{c_{max}}$  involved in the transport process depend on temperature.

In every case, the results were fitted on the whole temperature range with the relation

$$\ln(\gamma_{eff}/\gamma_0) = c_1 + c_2 T^{-\alpha}$$

where  $c_1$  and  $c_2$  are constants. This exponent  $\alpha$  is the same as the one of (1) since  $\gamma_{eff}$  is proportional to the conductivity of the system. When the numerical values of the various parameters increase or decrease by a factor of two, but with the same calculation hypotheses, the uncertainty on the value of the exponent  $\alpha$  can be estimated to  $\Delta\alpha = \pm 0.05$ . The value



**Figure 1.** (a)  $d$  and  $s$  are correlated,  $s/d = 0.06$ .  $d$  has a rectangular distribution with  $d_{min} = 20 \text{ \AA}$  and  $d_{max} = 500 \text{ \AA}$ .  $E_{cmax}$  and  $s_{max}$  do not depend on temperature.  $\alpha(1)$  has been estimated to be 0.65. (b)  $d$  and  $s$  are not correlated. The log-normal distribution of the charging energies (5b) is modified by random potentials (7) and (8).  $E_{cmax}$  and  $s_{max}$  do not depend on temperature.  $E_{cmax} = 200 \text{ meV}$ ,  $E_0 = 30 \text{ meV}$ ,  $E_{cmin} = 5 \text{ meV}$ ,  $s_{max} = 10 \text{ \AA}$ .  $\alpha(1)$  has been estimated to be 0.85. (c)  $d$  and  $s$  are not correlated.  $d$  and  $E_c$  are described by log-normal distributions (5b).  $E_{cmax}$  and  $s_{max}$  depend on temperature (13) and (14). We have chosen  $\beta = 1/2$  and

$$E_{cmax} = \left(\frac{E_0}{2}\right) T^{1/2} \quad s_{max} = \frac{34}{T^{1/2}}.$$

Reasonable orders of magnitude are obtained for  $s_{max}$  and  $E_{cmax}$  in the whole temperature range.  $E_0 = 20 \text{ meV}$ ,  $E_{cmin} = 5 \text{ meV}$ .  $\alpha(1)$  has been estimated to be 0.7. (d)  $d$  and  $s$  are not correlated. The log-normal distribution of the charging energies is modified by random potentials (7) and (8).  $E_{cmax}$  and  $s_{max}$  depend on temperature and  $\beta = 1/2$ .

$$E_{cmax} = \left(\frac{E_0}{2}\right) T^{1/2} \quad s_{max} = \frac{34}{T^{1/2}}.$$

$E_0 = 20 \text{ meV}$ ,  $E_{cmin} = 5 \text{ meV}$ .  $\alpha(1)$  has been estimated to be 0.5.

of the exponent  $\beta$  (13) and (14),  $1/4 \leq \beta \leq 1$ , does not affect significantly the value of the exponent  $\alpha$  obtained.

Several conclusions can be drawn from these simulations.

- The correlation  $s/d = \text{constant}$  is not necessary to ensure fractional exponents  $\alpha < 1$ .
- The value  $\alpha = 1/2$ , which is experimentally observed, is obtained when three conditions are fulfilled:

- (i)  $s$  and  $d$  are not correlated;
- (ii) random potentials are included in the charging energy distribution;
- (iii) the maximum intergrain distance and the maximum charging energy involved in the transport process depend on temperature.

Nevertheless, our results differ from the effective medium calculation reported by Adkins [7, 8].

According to Adkins, in the absence of any correlation between the particle separation,  $s$ , and the grain size,  $d$ , and with realistic distribution of  $s$  and  $E_c$  (or  $d$ ), the conduction at low temperatures is always very close to simple activation ( $\alpha = 1$ ). However, some of the assumptions used by Adkins seem to us oversimplified. To obtain an approximate

solution, Adkins replaces in (2a) the weighting factor  $[\gamma - \gamma_{eff}]/[\gamma - (d - 1)\gamma_{eff}]$  by its limits  $-1/d - 1$  corresponding to  $\gamma \ll \gamma_{eff}$  and 1 corresponding to  $\gamma \gg \gamma_{eff}$ . (2a) can then be written

$$\int_{\gamma_{eff}}^{\infty} f(\gamma) d\gamma = 1/d. \quad (16)$$

This equation is then solved graphically. This analysis suffers from one unsatisfactory feature. The effective medium treatment should be used only when the conductivity range involved is not too large and when the conductance distribution function,  $f(\gamma)$ , is rather peaked around  $\gamma_{eff}$ . Therefore, the conductances verifying the relations  $\gamma \gg \gamma_{eff}$  or  $\gamma \ll \gamma_{eff}$  should represent only a negligible part of the total distribution and the exact value of the weighting factor should be crucial to determine the conductivity. If the conductivity range is large, the percolation path method should be preferred. Seager and Pike [16] have indeed shown that the effective medium treatment gives better results if

$$\log \left( \frac{\gamma_{max}}{\gamma_{min}} \right) \leq 6 \quad (17)$$

where  $\gamma_{min}$  and  $\gamma_{max}$  are the maximum and minimum values of the conductances.

#### 4. Conclusion

In this work, we have simulated the thermal variation of the conductivity in granular systems with effective medium methods.

Hopping laws of the type  $\sigma(T) = \sigma_0 \exp(-(T_0/T)^\alpha)$  are obtained.

The exponent  $\alpha = 1/2$ , observed in many conducting polymers, is observed when the three following conditions are fulfilled:

- (i) the grain diameter,  $d$ , and the intergrain barrier,  $s$ , are not correlated;
- (ii) random potentials modify the charging energy distribution;
- (iii) the maximum intergrain barrier and the maximum charging energy involved in the transport process depend on temperature.

The existence of random potentials that would change the charging energy distribution needs further support and remains to be explained for conducting polymers.

#### References

- [1] Zuppiroli L, Bussac M N, Paschen S, Chauvet O and Forro L 1994 *Phys. Rev. B* **50** 5196
- [2] Zuo F, Angelopoulos M, MacDiarmid A G and Epstein A J 1987 *Phys. Rev. B* **36** 3475
- [3] Abeles B 1976 *Appl. Solid Sci.* **6** 1  
Abeles B, Sheng P, Coutts M D and Arie Y 1975 *Adv. Phys.* **24** 406
- [4] Sheng P, Abeles B and Arie Y 1973 *Phys. Rev. Lett.* **31** 44
- [5] Zhou M, Sheng P, Chen L and Abeles B 1992 *Phil. Mag. B* **65** 867
- [6] Sheng P and Klafter J 1983 *Phys. Rev. B* **27** 2583
- [7] Adkins C J 1982 *J. Phys. C: Solid State Phys.* **15** 7143
- [8] Adkins C J 1987 *J. Phys. C: Solid State Phys.* **20** 235
- [9] Sheng P 1992 *Phil. Mag. B* **65** 357
- [10] Bernasconi J 1973 *Phys. Rev. B* **7** 2252
- [11] Landauer R 1952 *J. Appl. Phys.* **23** 779  
Kirkpatrick S 1971 *Phys. Rev. Lett.* **27** 1722
- [12] Ambegaokar V, Halperin B I and Langer J S 1971 *Phys. Rev. B* **4** 2612
- [13] Granqvist C G and Buhrman R A 1976 *J. Appl. Phys.* **47** 2200  
Romanowski W and Krepinski L 1980 *Thin Solid Films* **65** 141



- [14] Pollak M and Adkins C J 1992 *Phil. Mag.* B **65** 855
- [15] Mostefa M and Olivier G 1987 *Solid State Commun.* **63** 219
- [16] Seager C H and Pike G E 1973 *Phys. Rev.* B **10** 1435