PHYSICAL REVIEW B VOLUME 27, NUMBER 4 15 FEBRUARY 1983

Hopping conductivity in granular disordered systems

Ping Sheng and J. Klafter
Corporate Research Science Laboratory, Exxon Research and Engineering Company, P. O. Box 45, Linden, New Jersey 07036
(Received 1 December 1982)

We study the temperature dependence of conductivity for high-resistivity granular disordered systems in terms of the critical-path method. It is shown that the low-field conductivity $\exp(-A/T^{\alpha})$ with $\alpha=\frac{1}{2}$ is obeyed over large temperature ranges with possible crossovers to $\alpha=\frac{1}{4}$ at low temperatures and to $\alpha>\frac{1}{2}$ at high temperatures. The temperatures at which the crossovers occur depend on the distribution of grain sizes. Comparisons are made with experiments and with other theoretical approaches.

In recent years, there is widespread experimental evidence[1-4] that the hopping conduction in disordered materials follows a temperature dependence of $-\ln\sigma \propto T^{-\alpha}$, where σ is the conductivity, T the temperature, and α a constant ranging from $\frac{1}{4}$ to 1.[5] Although the $\alpha=\frac{1}{4}$ [$\frac{1}{3}$ in two-dimensional (2D)] behavior has been justified in terms of variable range hopping proposed by Mott[6] and derived by Ambegaokar *et al.*,[7] the $\alpha=\frac{1}{2}$ temperature dependence, which has been observed in diverse granular systems with no apparent common feature, has no unique explanation. In this work we show that the whole range of the observed α values in granular systems can be understood in terms of a general theoretical model that gives $\alpha=\frac{1}{4}$ for $T\to 0$ and $\alpha>\frac{1}{2}$ (but <1) as $T\to\infty$. The interpolation between these limits then yields the widely observed $\alpha=\frac{1}{2}$ behavior over the intermediate temperature regime. However, the precise temperature range over which the $\alpha=\frac{1}{4}$ or $\alpha=\frac{1}{2}$ dependence appears is determined by the distribution of the conducting grain (or region) sizes.

We adopt the critical-path method (CPM)[7] as our basic approach to the analysis of the transport problem in random media characterized by random hopping distances and random grain energies. In CPM, one denotes by G_{ij} the conductance between any two localized sites (or two conducting grains) i and j. The conductance of the macroscopic medium is then determined by the following argument: Pick a value of conductance G and consider any two sites as connected if $G_{ij}\geq G$. If G is sufficiently large, the resulting connected sites will only form disjoint clusters. As G is lowered, however, the connected clusters are expected to increase in size until at $G=G_c$, the percolation conductance, an infinite network of connected sites is formed. Since G_c is the largest value of the conductance at which conduction over a continuous path becomes possible, it is identified as the macroscopic conductance of the sample and is assumed to dominate its temperature dependence. The hopping conduction is generally a problem of correlated bond-site percolation. In the CPM, however, correspondence is made with the bond percolation problem. G_c is then determined by the condition for bond percolation[8,9]: In a d-dimensional system, there should be on the average $b_c=d/(d-1)$ allowed bonds per grain (site).[8-10]

In order to calculate G_c through the average number of bonds per grain, one has to define G by considering the conduction mechanism. The electrical conduction in granular systems results from tunneling of electrons and holes from charged grains to neutral grains.[1,2,11] To generate the charge carriers, electrons have to be removed from one neutral grain to another. This process requires *at least* an energy E_c, which is the charging energy[1,2,11] $E_c=e^2/KD$, where e is the electronic charge, D is the grain size, and K is the dielectric constant of the inhomogeneous system. In the low-field limit, which we are interested in here, the charge carriers are thermally activated; the conductance G_{ij} between two grains i and j is then[7-9]

$$G_{ij}=G_0\exp(-2\chi S_{ij}-E_{ij}/kT)\ , \tag{1}$$

where χ is the tunneling parameter,

$$E_{ij}=\tfrac{1}{2}(|E_i-E_j|+|E_i|+|E_j|)\ ,$$

and S_{ij} denotes the distance between the grain surfaces along the line joining their centers (tunneling distance).

We now return to the percolation argument. The condition $G_{ij}\geq G_c$ is expressed as[7-9]

$$\frac{S_{ij}}{S_m}+\frac{1}{2}\frac{|E_i|+|E_j|+|E_i-E_j|}{E_m}\leq 1\ , \tag{2}$$

where $S_m=(1/2\chi)\ln(G_0/G_c)$ and $E_m=kT\ln(G_0/G_c)$. S_m and E_m are the maximum tunneling distance and the maximum energy that any initial or final state can have, so that $G_{ij}\geq G_c$. Equation (2) defines a corre-

lation between the S_{ij} and the E_i, E_j that construct the connected bonds.

From the above discussion, it is clear that the formation of the critical path requires the following equation to be satisfied:

$$b_c = \frac{\int_{-E_m}^{E_m} dE_i \rho(E_i) \int_{-E_m}^{E_m} dE_j \rho(E_j) \int_0^{S_a(E_i,E_j)} dS_{ij} \int_0^{\infty} dr_{ij}\, 4\pi r_{ij}^2 g(r_{ij}) \delta\left(r_{ij} - \frac{D_i + D_j}{2} - S_{ij}\right)}{\int_{-E_m}^{E_m} dE_i \rho(E_i)} . \tag{3}$$

Here $\rho(E)$ is the density of states, $S_a(E_i,E_j)$ is the maximum allowed non-negative value of S_{ij} satisfying the inequality (2) for a given set of E_i and E_j, r_{ij} is the center-to-center separation between particles i and j, and

$$g(r_{ij}) = \begin{cases} N, & r_{ij} > \dfrac{D_i + D_j}{2} \\ 0, & r_{ij} \leq \dfrac{D_i + D_j}{2} \end{cases}$$

is the hard-sphere correlation function, where N denotes the number of particles per unit volume. The integral over r_{ij} in Eq. (3) is required to give the probability that, over all the possible separation r_{ij} between two spherical grains of diameters D_i and D_j, there is a tunneling distance S_{ij}. The factor $4\pi r_{ij}^2 dr_{ij}$ gives the volume in which the center of the second grain can sit, and $g(r_{ij})$ is the probability that there is a grain at distance r_{ij} away from the grain i. The use of $\delta(r_{ij} - (D_i + D_j)/2 - S_{ij})$ in relating the r_{ij} to S_{ij} neglects the possible intrusions of other grains into the path of tunneling between grains i and j. Such a simplification is justified since, in the estimate of the critical-path conductance, one always calculates the lower bound of G_{ij},[7] which this approximation gives. Carrying out the r_{ij} and the S_{ij} integrations and approximating $(D_i + D_j)/2$ by the average diameter D_0, we get

$$b_c = N \frac{\int_{-E_m}^{E_m} dE_i \rho(E_i) \int_{-E_m}^{E_m} dE_j \rho(E_j) \frac{4\pi}{3} (S_a^3 + 3S_a^2 D_0 + 3S_a D_0^2)}{\int_{-E_m}^{E_m} dE_i \rho(E_i)} . \tag{4}$$

For the case of point impurities ($D_0 = 0$) and constant $\rho(E)$, Eq. (4) can easily be written in the form as obtained by Shante[9]:

$$b_c = E_m S_m^3 f , \tag{5}$$

where f is a constant. From Eq. (5) the $\ln G_c \sim -T^{-1/4}$ relation of 3D variable range hopping is directly recovered. This result should be contrasted with the theory of Simanek,[12] where the assumption of a constant $\rho(E)$ and equal probability for all tunneling distances S_{ij} leads to $\ln G_c \sim -T^{-1/2}$.

In order to carry out the calculation for random systems with conducting grains (or regions), we have to consider the role of charging energy and its relation to $\rho(E)$. Since the charging energy E_c is just the capacitance energy required to put/remove a charge on/from a neutral conducting grain, it defines the minimum energy a charge carrier can have on any given grain. For a typical grain, the existence of the charging energy therefore implies that the density of states for the grain has the form $\rho_s(E) = \Theta(E - E_c)/\bar{\Delta}$, where $\bar{\Delta}$ is the average electronic level separation inside conducting grains, and $\Theta(E)$ is the step function. Generally, $\bar{\Delta}$ might be energy dependent, which will modify $\rho(E)$ but will not effect our conclusions. To obtain $\rho(E)$ for an assembly of grains, we have to integrate $\rho_s(E)$ with the distribution of E_c, $P(E_c)$. If we assume a log-normal distribution for the size of the grains,[13] then $P(E_c)$ will also be a log-normal distribution

$$P(E_c) = \frac{1}{\sqrt{2\pi}} \frac{1}{\ln\mu} \exp\left[-\frac{[\ln(E_c/E_0)]^2}{2(\ln\mu)^2}\right] \frac{1}{E_c} , \tag{6}$$

where μ is the parameter controlling the width of the distribution, and $E_0 \equiv e^2/KD_0$ is the most probable value of E_c. Given $P(E_c)$ we get, for the density of states of the grains $\rho_G(E)$,

$$\rho_G(E) = \frac{1}{\bar{\Delta}} \int_0^E \Theta(E - E_c) P(E_c)\, dE_c = \frac{1}{\bar{\Delta}} \int_0^E P(E_c)\, dE_c . \tag{7}$$

It should be noted that for $E = 0$, $\rho_G(E) = 0$. However, in a composite material there could be states other than those in the conducting grains. For example, there may be impurities which would contribute a finite density of states at $E = 0$ so that at the Fermi level these states, instead of those inside the grains, would give the main contribution to conduction. There is some experimental evidence[14] that $\rho(E)$ indeed has a nonzero value at $E = 0$. Assuming that there is a constant density of state ρ_0 due to these

states, we get $\rho(E)$ as

$$\rho(E)=\rho_G(E)+\rho_0 \ . \tag{8}$$

Qualitatively, $\rho(E)$ has the behavior of increasing from ρ_0 at $E=0$ to about $\rho_0+1/2\bar{\Delta}$ at $|E|=E_0$. For $|E|>E_0$, $\rho(E)$ slowly approaches the asymptotic value of $\rho_0+(1/\bar{\Delta})$. Using this form of $\rho(E)$ and changing variables to $e=E/E_m$, $s=S_a/S_m$, we get

$$b_c=8x\frac{\int_{-1}^{1}de_i\rho(|e_i|kTY/E_0)\int_{-1}^{1}de_j\rho(|e_j|kTY/E_0)\left[\left(\frac{sYE_0}{2C_0(x)}+1\right)^3-1\right]}{\int_{-1}^{1}de_i\rho(|e_i|kTY/E_0)} \ . \tag{9}$$

Here $Y=\ln(G_0/G_c)$, $x=ND_0^3\pi/6$ is the volume fraction of the conducting grain,

$$s=[1-\tfrac{1}{2}(|e_i|+|e_j|+|e_i-e_j|)]\Theta(s) \ ,$$

$$C_0(x)=\frac{e^2\chi}{K}=\frac{\eta[(\pi/6x)^{1/3}-1]}{(\pi/6x)^{1/3}-0.5} \ ,$$

$\eta=e^2\chi/\epsilon$, ϵ being the dielectric constant of the insulator, and the absolute value of e_i and e_j is taken because we are assuming symmetry in the distribution of positively and negatively charged grains. By using $b_c=1.5$,[9] $\eta=3.8$ eV,[15] $\bar{\Delta}\simeq 1$ meV, $\rho_0\simeq 0.1/\bar{\Delta}$, $E_0\simeq 20$ meV (~ 150-Å grains),[2] we plot in Fig. 1 the calculated Y as a function of T and x for two values of μ. For $\mu=1.6$, which corresponds to a distribution where the maximum grain size is about a factor $(1.6)^2=2.56$ times the minimum grain size, it is seen that $-\ln G_c$ behaves as $T^{-1/2}$ over a significant temperature range. It should be especially remarked that for $x=0.5$, the $\alpha=\frac{1}{2}$ temperature dependence holds from $T\cong 2$ to 400 K, which reproduces the experimental results of Chui *et al.*[3] over the same temperature range with about the same slope (better fit can be obtained by fine tuning the value of x). The experimental grain size distribution in this case is measured to vary, from minimum to maximum, by roughly a factor of 3,[3] which is in accord with our theoretical value of ~ 2.6. For $\mu=3$, which corresponds to a broad distribution of grain sizes, the $\alpha=\frac{1}{2}$ behavior is valid over even larger temperature ranges. To explain such $T^{-1/2}$ temperature dependence, we note that the $T\to 0$ and $T\to\infty$ limiting behaviors of $-\ln G_c$ can easily be deduced from Eqs. (4) and (9) as $\alpha=\frac{1}{4}$ and $\alpha>\frac{1}{2}$ (but less than 1), respectively.[16] The $\alpha=\frac{1}{2}$ dependence then results from interpolation between these limiting behaviors over the intermediate temperature range. In contrast to the theory of Efros *et al.*, which produces the $\alpha=\frac{1}{2}$ behavior by postulating that $\rho(E)\propto E^2$ as a consequence of the electron-electron interaction, the results of the present theory are insensitive to the exact form of $\rho(E)$. In addition, our theory does not give just the $\alpha=\frac{1}{2}$ behavior. By varying the value of E_0, it is found that decreasing the grain size (increasing E_0) has the effect of extending the $\alpha=\frac{1}{4}$ behavior to higher temperatures, thereby making $\alpha=\frac{1}{4}$ perhaps a better overall fit than $\alpha=\frac{1}{2}$ for samples with small grain sizes. On the other hand, increasing the grain size (decreasing E_0) has the effect of extending the $\alpha\geq\frac{1}{2}$ behavior to lower temperatures. Such size dependent results have been recently reported for conductivities in doped polyacetylenes.[4] Yet if μ is large (such as $\mu=3$), the resulting overall behavior would still appear as $\alpha=\frac{1}{2}$, with only minor change in the slope. This is consistent with the results of the annealing experiments by Abeles *et al.*[2] As a further comparison between theory and experiment, we plot in Fig. 2 the slope of the straight-line portion for the $-\ln G_c$ vs $T^{-1/2}$ curve

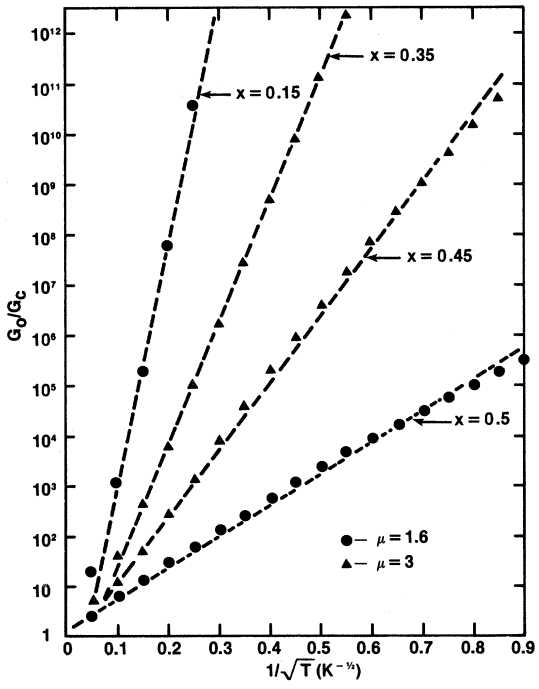

FIG. 1. $\ln(G_0/G_c)$ plotted as a function of $1/\sqrt{T}$. Numerically calculated values are denoted by ● ($\mu=1.6$) and ▲ ($\mu=3$). Dashed straight lines are for aid to visualization.

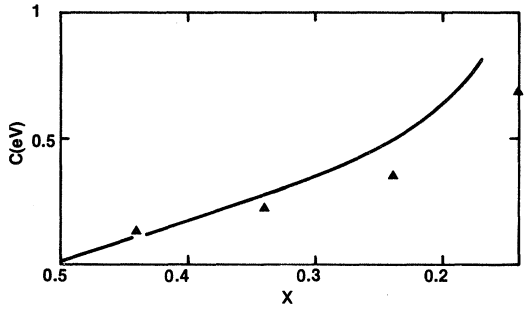

FIG. 2. Plot of C, where $C = kT(\ln G_0/G_c)^2$, as a function of x. The solid line is calculated for $\mu = 3$ and the parameters given in the text. Experimental data are for $NiSiO_2$ (Ref. 2).

as a function of x. The experimentally measured results for granular metals are shown on the same graph. It is seen that the agreement is good.

The derivation we presented here follows the arguments given in Refs. 1 and 2. However, we have relaxed the correlation assumption between charging energies and the tunneling distances used in the previous work.[1,2]

To summarize, we have developed a general theoretical model in which the temperature dependence of hopping conduction in various random systems can be considered in a unified framework. Comparison with experiments yields very good agreements. The electric field dependence of the model, and other theoretical considerations, will be published elsewhere.

[1]Ping Sheng, B. Abeles, and Y. Arie, Phys. Rev. Lett. 31, 44 (1973).

[2]B. Abeles, Ping Sheng, M. D. Coutts, and Y. Arie, Adv. Phys. 24, 407 (1975).

[3]T. Chui, G. Deutscher, P. Lindenfeld, and W. L. McLean, Phys. Rev. B 23, 6172 (1981).

[4]E. K. Sichel, M. Knowles, M. Rubner, and J. Georger, Jr., Phys. Rev. B 25, 5574 (1982).

[5]C. J. Adkins (unpublished).

[6]N. F. Mott, Philos. Mag. 19, 835 (1969).

[7]V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B 4, 2612 (1971).

[8]V. K. Shante, Phys. Lett. 43A, 249 (1973).

[9]V. K. Shante, Phys. Rev. B 16, 2597 (1977).

[10]G. E. Pike and C. H. Seager, Phys. Rev. B 10, 1421 (1979). For a 3D lattice $b_c = \frac{3}{2}$. In the case of an amorphous material b_c approaches the limiting value of 2.8.

[11]C. A. Neugebauer and M. B. Webb, J. Appl. Phys. 33, 74 (1962).

[12]E. Simanek, Solid State Commun. 40, 1021 (1981).

[13]C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. 47, 2200 (1976).

[14]J. W. Gardner and C. J. Adkins, Physica (Utrecht) 107B, 419 (1981).

[15]It should be noted that the definition of η differs from that of Ref. 2 by a factor of 2.

[16]At low temperatures, hopping occurs over large distances and between sites that are close to the Fermi level. That implies $\rho(E) \simeq \rho_0$ and

$$[(sYE_0/2C_0)+1]^3 - 1 \approx (sYE_0/2C_0)^3 ,$$

and the problem becomes exactly identical to that of variable range hopping, with $\alpha = \frac{1}{4}$. At high temperatures, hopping is between nearest neighbors with $E > E_0$. This means $\rho(E)$ is in the monotonically increasing regime, and

$$[(sYE_0/2C_0)+1]^3 - 1 \approx 3sYE_0/2C_0 .$$

If we assume $\rho(E)$ behaves as E^β with $\beta \geq 0$ in the same range of E, then we can write

$$b_c = E_m^{\beta+1} S_m \text{ (constant)} \propto (kT)^{\beta+1} Y^{\beta+2} .$$

From this equation we get $\alpha = (\beta+1)/(\beta+2)$ in the high-temperature regime.