

Concentration dependence of hopping conductivity in granular metals

G. A. Levin

*Akademicheskaya 2-A, Kv. 415, Novosibirsk 630072, U.S.S.R.**

(Received 20 December 1985)

An analysis of conductivity in a model of identical metallic spheres randomly distributed in an insulator is presented. Using an approach based on ideas of percolation theory, the equation is derived which defines the limiting value for the separations between neighboring particles along the "optimal path." The volume and structure of the current-carrying backbone are discussed and its contribution to the bulk conductivity is obtained.

Granular metals are inhomogeneous materials consisting of metallic particles dispersed in an insulator. For metal concentrations above the percolation threshold, a network of continuous current-conducting routes is present and the bulk conductivity is of metallic type. Below threshold the continuous metallic paths are absent and electrical transport results from thermally activated tunneling of electrons between isolated metallic grains. (See the review of Abeles *et al.*¹)

However, the existence of a metal-insulator transition influences the parameters of hopping conductance at concentrations below the critical value. In the vicinity of the transition the system is "prepared" for the appearance of an infinite cluster with the result that infinite "optimal paths" exist in the material, which are characterized by maximum charge mobility. The charge-exchange rate between two grains, defining the mobility, is given by

$$v \sim \exp(-2\chi S_{ij} - W_{ij}/kT), \quad (1)$$

where S_{ij} is the separation between the surfaces of the grains, χ is the tunneling factor, and W_{ij} is the activation energy.^{2,3} Consequently, in order to evaluate the mobility we must obtain the limiting values for S_{ij} and W_{ij} along the optimal routes.

For this purpose we consider a model of identical metal spheres randomly distributed in an insulator matrix. Let a be the diameter of spheres and ϕ be the volume fraction of metal,

$$\phi = \frac{\pi}{6} a^3 n, \quad (2)$$

where n is the number density of metal particles.

Consider the following thought experiment. Without changing the number of grains and their positions we shall increase their diameters until the effective composition reaches the critical value ϕ_c . Given this condition an infinite cluster consisting of adjoining or overlapping contours of swollen particles arises. It is known that the infinite cluster contains a current-conducting "backbone" and "tag ends" which carry no current.^{4,5}

We call a "virtual backbone" the aggregate of grains which should transform into the real backbone under such a simultaneous swelling of all metallic constituents.

It is evident that all separations between neighboring particles which make up the virtual backbone do not

exceed the value $S = b - a$, where b is the diameter of the swollen grains. Along any other path there are sections where the hopping distance is greater than S .

In the first approximation the condition for the appearance of the infinite cluster may be written in the form

$$\frac{\pi}{6} b^3 n = \phi_c, \quad (3)$$

where n is given by Eq. (2) and ϕ_c is the percolation threshold. According to percolation theory and effective-medium theory the value of the critical concentration in 3D systems lies in the range 0.3–0.33.^{6,7} From Eq. (3) we have

$$S \equiv b - a = a \left[\left(\frac{\phi_c}{\phi} \right)^{1/3} - 1 \right]. \quad (4)$$

However, Eq. (3) is not exact because it does not take into account the overlapping of the contours of swollen particles. Because of this overlapping, the effective volume of a grain, defining the concentration of the "metallic phase," becomes less than the volume of a sphere of diameter b [see Fig. 1(a)]. If r is the distance between the centers of two overlapping spheres ($a \leq r \leq b$), the effective volume of each is equal to

$$\frac{\pi}{6} b^3 - \Delta V, \quad (5)$$

where

$$\Delta V(r) = \frac{\pi}{8} [b(b-r)^2 - \frac{1}{3}(b-r)^3] \quad (6)$$

is the volume of a spherical segment. If a given particle has a few neighbors, whose centers lie at distances r_1, \dots, r_n from its center, the "defects of volume" are summed, so that

$$\Delta V = \Delta V(r_1) + \dots + \Delta V(r_n). \quad (7)$$

Let us introduce the radial distribution function $g(r)$ for the system of hard spheres. The quantity $ng(r)$ defines the number density of particles whose centers lie at a distance r from the center of a given particle. By virtue of Eqs. (5) and (7), we must write the following instead of Eq. (3):

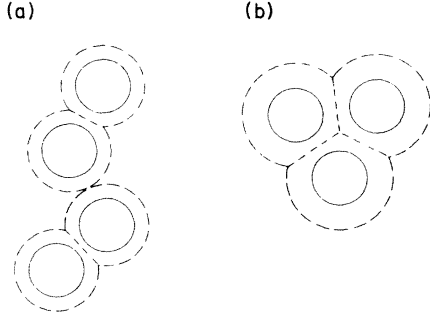


FIG. 1. Schematic illustration of identical metal spheres randomly distributed in an insulating matrix. Solid lines are spheres of diameter a , at a concentration below the percolation threshold; dotted lines denote swollen spheres of diameter b at the critical concentration for percolation. Two cases are shown: (a) $b \leq 2a/\sqrt{3}$; (b) $b > 2a/\sqrt{3}$.

$$n \left[\frac{\pi}{6} b^3 - 4\pi n \int_a^b g(r) \Delta V(r) r^2 dr \right] = \phi_c, \quad (8)$$

where $\Delta V(r)$ is given by Eq. (6). This equation remains true at all concentrations for which $b \leq 2a/\sqrt{3}$, because at $b > 2a/\sqrt{3}$ there are configurations disturbing the validity of Eq. (7) [see Fig. 1(b)]. The radial distribution function for rigid spheres has been the subject of many investigations and there are good analytical approximations for $g(r)$ at concentration $\phi \leq 0.3$.^{8,9}

Near the transition, when $b - a \ll a$, we can simplify Eq. (8),

$$b^3 - \pi n g(a) b^3 (b - a)^3 = \frac{\phi_c}{\phi} a^3. \quad (9)$$

Here $g(a)$ is the value of $g(r)$ corresponding to two spheres in contact when their centers are separated by the distance a . Seeking the solution of Eq. (9) in the form $b = b^{(1)} + b^{(2)}$, where $b^{(1)}$ is given by expression (4) and $b^{(2)} \ll b^{(1)}$, we obtain

$$S = a \left[\left[\frac{\phi_c}{\phi} \right]^{1/3} - 1 \right] \left\{ 1 + 2g(a)\phi_c \left[1 - \left[\frac{\phi}{\phi_c} \right]^{1/3} \right]^2 \right\}. \quad (10)$$

For $g(a)$ one can use the interpolation formula proposed by Carnahan and Starling,¹⁰

$$g(a) = [4 - 2\phi] / [4(1 - \phi)^3].$$

The replacement of $g(r)$ in Eq. (8) by the constant $g(a)$ yields the interpolation of Eq. (8), which becomes exact as $\phi \rightarrow \phi_c$ and $\phi \rightarrow 0$ [in the latter case because $g(r) \rightarrow 1$],

$$x^3 - 6\phi g(a) x^3 (x - 1)^3 \left[1 - \frac{7}{4} \left[1 - \frac{1}{x} \right] + \left[1 - \frac{1}{x} \right]^2 - \frac{1}{6} \left[1 - \frac{1}{x} \right]^3 \right] = \frac{\phi_c}{\phi}, \quad (11)$$

where $x \equiv b/a$. The numerical solution of Eq. (11) is shown in Fig. 2. Its asymptotic form at $x \gg 1$ is

$$x \approx \left[\frac{m}{\phi} \right]^{1/3}, \quad m = 1 - \sqrt{1 - 2\phi_c} \approx 0.367 - 0.417.$$

By similar arguments for a two-dimensional system of hard disks the equation for the critical diameter b may be written

$$n \left[\frac{\pi}{4} b^2 - 2\pi n \int_a^b g(r) \Delta V(r) r dr \right] = \phi_c, \quad (12)$$

$$\Delta V(r) = \frac{b^2}{4} \left[\frac{\pi}{2} - \arcsin \left[\frac{r}{b} \right] - \frac{r}{b} \left[1 - \frac{r^2}{b^2} \right]^{1/2} \right]$$

$$\approx \frac{\sqrt{2}}{3} b^2 \left[1 - \frac{r}{b} \right]^{3/2},$$

where $n = 4\phi/\pi a^2$ and $\phi_c = 0.5$.

Near threshold Eq. (12) takes the form

$$b^2 - \frac{16\sqrt{2}}{15} n g(a) b^4 \left[1 - \frac{a}{b} \right]^{5/2} = \frac{\phi_c}{\phi} a^2,$$

where¹¹

$$g(a) = \frac{1 - \frac{7}{16}\phi}{(1 - \phi)^2}.$$

This has the solution

$$S = a \left[\left[\frac{\phi_c}{\phi} \right]^{1/2} - 1 \right] \times \left\{ 1 + \frac{2\sqrt{2}}{\pi} g(a)\phi_c \left[1 - \left[\frac{\phi}{\phi_c} \right]^{1/2} \right]^{3/2} \right\}. \quad (13)$$

Equations (8) and (12) are exact for $b \leq 2a/\sqrt{3}$. This corresponds to the conditions $\phi \geq 0.65$, $\phi_c \approx 0.19$ for 3D systems ($\phi_c = 0.3$) and $\phi \geq 0.75$, $\phi_c = 0.37$ for 2D systems ($\phi_c = 0.5$). It is easy to convince oneself from Fig. 1(b)

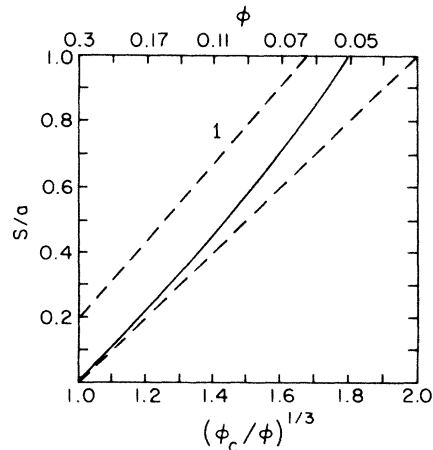


FIG. 2. Solid curve represents the solution of Eq. (8) and the broken line (1) represents the relation $S/a = (\pi/6\phi)^{1/3} - 1$.

that at $b > 2a/\sqrt{3}$, the true values of $\Delta V(r)$ which must be substituted into Eqs. (8) and (12) are less than those given by expressions (6) and (12). Consequently, the true values of S are slightly less than those from expressions (10) and (13), but greater than $S^{(1)} = a[(\phi_c/\phi)^{1/d} - 1]$. It should be noted that the deviation from the $\phi^{-1/d}$ law resulting from impermeability of metallic grains is relatively small. Thus at $(\phi_c/\phi)^{1/3} = 2$ the ratio $S/S^{(1)} < 1.16$ and for disks at $(\phi_c/\phi)^{1/2} = 2$, the ratio $S/S^{(1)} < 1.19$.

Let us consider the energy-dependent part of the conductance between two grains. The process of charge transfer requires a certain amount of charging energy. Following Abeles *et al.*¹ we shall approximate the charging energy by the energy of a spherical capacitor with internal diameter equal to a and with the gap between plates equal to the separation λ between a given particle and its nearest neighbor. From electrostatic theory

$$W = \frac{\epsilon}{8\pi} \int |\mathbf{E}|^2 dV = \frac{\epsilon}{2} \int_{a/2}^{a/2+\lambda} \left[\frac{e}{\epsilon r^2} \right]^2 r^2 dr = \frac{e^2}{\epsilon a} \frac{\lambda}{\frac{a}{2} + \lambda}. \quad (14)$$

Here ϵ is the dielectric constant of the insulator and e is the electron charge.

We now turn to the calculation of the bulk conductivity and consider for this purpose the charge transfer along the paths of greatest mobility, i.e., along the virtual backbone (VB). The structure of the VB coincides, by definition, with the structure of a "real" backbone consisting of "swollen" grains. When the effective composition exceeds the percolation threshold by a small amount, the backbone is a sparse network of thin channels.^{5,12} Consequently, the VB may be approximately considered as a network of one-dimensional chains. In a small electric field the current along the chain is defined by the charge mobility μ or, by virtue of the Einstein relation, by the diffusion coefficient D ($\mu = D/kT$).

To calculate the diffusion coefficient we shall use the following master equation:

$$\frac{dP_j}{dt} = \nu_{j-1}(P_{j-1} - P_j) + \nu_j(P_{j+1} - P_j).$$

P_j is the probability for the electron or "hole" to be on grain j at time t and the conductances ν_j are independent random variables. If the ν_j are distributed according to a probability density $\rho(\nu)$, we may use the well-known expression for the diffusion constant¹³

$$D^{-1} = \frac{1}{b^2} \int \rho(\nu) \frac{d\nu}{\nu}, \quad (15)$$

where b is the distance between the centers of grains. The conductance between nearest-neighbors is determined by the separation λ and, according to the expressions (1) and (14), it takes the form

$$\nu(\lambda) = \nu_0 \exp \left[-2\chi\lambda - \frac{e^2}{\epsilon a k T} \frac{\lambda}{\left[\frac{a}{2} + \lambda \right]} \right]. \quad (16)$$

The separations along the VB are independent random parameters distributed in a range $0 \leq \lambda \leq S$ with the probability density

$$q(\lambda) = z^{-1} u \Theta(S - \lambda). \quad (17)$$

Here $\Theta(x)$ is the Heaviside step function and the limiting value S is the solution of Eq. (8). The normalization constant z is determined from the condition

$$\int q(\lambda) d\lambda = 1,$$

and $u(\lambda)$ is the probability that there are no centers of neighboring particles inside the spherical layer of radius a and thickness λ , circumscribed around the center of a given particle. This probability may be evaluated by the Poisson distribution

$$u(\lambda) = e^{-\langle N \rangle}, \quad (18)$$

where

$$\langle N \rangle = 4\pi n \int_a^{a+\lambda} g(r) r^2 dr \approx 4\pi n g(a) a^2 \lambda = 24\phi g(a) \frac{\lambda}{a}.$$

The same result for $u(\lambda)$ may be obtained from thermodynamics as the probability for the creation of a cavity around a given particle in a gas of hard spheres.⁸

Finally, we have

$$q(\lambda) = \frac{\beta e^{-\beta\lambda}}{1 - e^{-\beta S}} \Theta(S - \lambda), \quad \beta = \frac{24\phi g(a)}{a}. \quad (19)$$

Let us introduce the function

$$\mathcal{N}(\nu) = \int_0^\nu \rho(\nu') d\nu', \quad (20)$$

which, on the other hand, may be represented as

$$\mathcal{N}(\nu) = \int q(\lambda) \Theta(\nu - \nu(\lambda)) d\lambda. \quad (21)$$

Thus, we have

$$\rho(\nu) = \frac{d\mathcal{N}(\nu)}{d\nu} = \int q(\lambda) \delta(\nu - \nu(\lambda)) d\lambda. \quad (22)$$

Substituting this in (15) one finds

$$D^{-1} = \frac{1}{b^2} \int \frac{q(\lambda)}{\nu(\lambda)} d\lambda = \frac{1}{\nu_0 b^2} \frac{\beta(e^{-(\alpha-\beta)S} - 1)}{(\alpha-\beta)(1 - e^{-\beta S})}, \quad \alpha = 2\chi + \frac{2e^2}{\epsilon a^2 k T}. \quad (23)$$

In a small electric field \mathbf{E} , the mean current in a one-dimensional chain is of the form

$$|i| \sim e^2 n_1 \mu |\mathbf{E}|, \quad (24)$$

where n_1 is the number density of grains per unit length. Let n_2 be a number density of current-carrying chains intersecting the plane normal to the applied field. The current density $j = n_2 i$, and taking into account that $n_1 n_2 \sim n_b$ where n_b is the number density of grains belonging to the VB, we obtain for the bulk conductivity the following expression:

$$\sigma \sim \frac{e^2 v_c b^2 n_b}{kT} \frac{\alpha - \beta}{\beta} \frac{1 - e^{-\beta S}}{e^{(\alpha - \beta)S} - 1}. \quad (25)$$

In order to obtain the value of n_b one must return to Eqs. (3) and (8). In fact, on the right-hand sides of these equations we must replace the percolation threshold ϕ_c by the constant $\phi' > \phi_c$ and define it from the condition of maximization of conductivity. Let $\phi' = \phi_c + \delta\phi$ and $\delta\phi \ll \phi_c$. Then we have

$$\begin{aligned} n_b &\sim n \left[\frac{\delta\phi}{\phi_c} \right]^{t_1}, \\ S' &= a \left[\left[\frac{\phi'}{\phi} \right]^{1/3} - 1 \right] \\ &\approx a \left[\left[\frac{\phi_c}{\phi} \right]^{1/3} - 1 \right] \frac{1}{3} a \left[\frac{\phi_c}{\phi} \right]^{1/3} \frac{\delta\phi}{\phi_c}. \end{aligned} \quad (26)$$

The exponent $t_1 = 1.7 - 2$ and the optimal value of $\delta\phi$ is derived by the maximization of the expression

$$\left[\frac{\delta\phi}{\phi_c} \right]^{t_1} \exp \left[-\frac{1}{3} \alpha_1 b \frac{\delta\phi}{\phi_c} \right], \quad \alpha_1 \equiv \alpha - \beta.$$

This yields

$$\frac{\delta\phi}{\phi_c} = \frac{3t_1}{\alpha_1 b}. \quad (27)$$

Using the typical parameters of granular metals¹

$$\chi = 0.5 \text{ \AA}^{-1}, \quad \gamma = 2\chi e^2 / \epsilon \sim 3 \text{ eV}, \quad kT \sim 10^{-2} \text{ eV},$$

and $a \sim 20 \text{ \AA}$, we obtain

$$\begin{aligned} \alpha &= \chi \left[2 + \frac{\gamma}{kT(\chi a)^2} \right] \sim 2.5 \text{ \AA}^{-1}, \\ b &= a \left[\frac{\phi_c}{\phi} \right]^{1/3} \gtrsim 20 \text{ \AA}. \end{aligned} \quad (28)$$

Taking into account that at $\phi \leq 0.3$, the values of $g(a) \leq 2$ and $\beta \leq 0.7 \text{ \AA}^{-1}$, we get $\delta\phi/\phi_c \leq 0.1$, $n_b/n \leq 0.01$. This evaluation confirms the initial supposition about the structure of the VB in granular metals as a sparse network

of thin channels, among which at least the most "difficult" sections are sufficiently long one-dimensional chains. Finally, the contribution of the VB to the bulk conductivity is given by

$$\sigma \sim \frac{e^2 n v_0 a^2}{kT} \left[\frac{\phi_c}{\phi} \right]^{2/3 - t_2} \frac{\alpha_1}{\beta(\alpha_1 a)^{t_1}} \frac{1 - e^{-\beta S}}{e^{\alpha_1 S} - 1}. \quad (29)$$

Let us compare this value with the contribution resulting from the spatially uniform transport of charges through the material. In this case the mean separation is greater than in the VB, but the number of grains involved in the current flow is also greater. For a simple cubic lattice the separation

$$S_0 = a \left[\left[\frac{\pi}{6\phi} \right]^{1/3} - 1 \right]$$

and the contribution of the uniform current to the bulk conductivity may be evaluated as

$$\sigma_{\text{un}} \sim \frac{e^2 n v_0 b_0^2}{kT} e^{-\alpha S_0}. \quad (30)$$

From Fig. 2 one can see that $S_0 - S \sim 0.2a$ and, by using the parameters of the material given above, we obtain

$$\frac{\sigma}{\sigma_{\text{un}}} \sim \frac{n_b}{n} \exp[\alpha(S_0 - S)] \gg 1. \quad (31)$$

Thus, one may conclude that in granular metals in a hopping-conductivity regime the spatial distribution of current is highly nonuniform and it flows through the relatively small number of optimally arranged particles. The parameters of this system of grains (separations and activation energy) are essentially different from those obtained by averaging over the volume and they cannot be obtained directly from structural investigations.

A comparison with real metals may be carried out only for samples which have sufficient uniformity of constituent sizes, and a purely activated-type temperature dependence for the conductivity.

*Requests for reprints should be addressed to the author, with copies to M. P. Sarachik, Physics Department, City College, Convent Avenue and 138 Street, New York, N.Y. 10031.

¹B. Abeles, Ping Sheng, D. Coutts, and Y. Arive, *Adv. Phys.* **24**, 407 (1975).

²C. A. Neugebauer and M. B. Webb, *J. Appl. Phys.* **33**, 74 (1962).

³C. J. Adkins, *J. Phys. C* **15**, 7143 (1982).

⁴A. S. Skal and B. I. Shklovskii, *Fiz. Tekh. Poluprovodn.* **8**, 1586 (1974) [*Sov. Phys.—Semicond.* **8**, 1029 (1975)].

⁵S. Kirkpatrick, *Electrical Transport and Optical Properties of Inhomogeneous Media*, (Ohio State University, 1977), Proceedings of the Conference on Electrical Transport and Optical Properties of Inhomogeneous Media, AIP Conf. Proc.

No. 40, edited by J. C. Garland and D. B. Tanner (AIP, New York, 1978), p. 99.

⁶S. Kirkpatrick, *Rev. Mod. Phys.* **45**, 574 (1973).

⁷R. Landauer, *J. Appl. Phys.* **23**, 779 (1952).

⁸J. A. Barker and D. Henderson, *Revs. Mod. Phys.* **48**, 587 (1976).

⁹B. B. Deo and A. C. Naik, *Phys. Rev. A* **28**, 1700 (1983).

¹⁰N. P. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).

¹¹D. Henderson, *Mol. Phys.* **30**, 971 (1975).

¹²B. I. Shklovskii and A. L. Efros, *Usp. Fiz. Nauk.* **117**, 401 (1975) [*Sov. Phys.—Usp.* **18**, 845 (1975)].

¹³R. Zwanzig, *J. Stat. Phys.* **28**, 127 (1982).