Critical Percolation and Transport in Nearly One Dimension

A. N. Samukhin,[1,2] V. N. Prigodin,[1,3] and L. Jastrabík[2]
[1]*A. F. Ioffe Physical & Technical Institute, 194021 St. Petersburg, Russia*
[2]*Institute of Physics AS CR, Na Slovance 2, 180 40 Prague 8, Czech Republic*
[3]*Max-Plank-Institute für Physik Komplexer Systeme, Aussenstelle Stuttgart, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
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A random hopping on a fractal network with dimension slightly above 1, $d = 1 + \epsilon$, is considered as a model of transport for conducting polymers with nonmetallic conductivity. Within the real space renormalization group method of Migdal and Kadanoff, the critical behavior near the percolation threshold is studied. In contrast to a conventional regular expansion in ϵ, the critical indices of correlation length, $\nu = \epsilon^{-1} + O(e^{-1/\epsilon})$, and of conductivity, $t \simeq \epsilon^{-2}\exp(-1 - 1/\epsilon)$, are found to be nonanalytic functions of ϵ as $\epsilon \to 0$. In the case of variable range hopping a "1D Mott's law" $\exp[-(T_t/T)^{1/2}]$ dependence was found for the dc conductivity. It is shown that the same type of strong temperature dependence is valid for the dielectric constant and the frequency-dependent conductivity, in agreement with experimental data for poorly conducting polymers. [S0031-9007(96)01916-3]

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Conducting polymers represent a large class of new materials with a great variety of transport properties [1]. The room-temperature conductivity (σ_{RT}) of some of them attains the metallic value, and the temperature and frequency dependencies of their conductivity are closely to be metallic. The nature of the metallic phase is presently the subject of intensive study [2]. One point is that the metallic state is provided by strong interchain coupling in these materials [3]. In polymers with moderate σ_{RT} (of the order of several hundreds S/cm) the conductivity, as a rule, decreases with decreasing temperature. Because this decay follows a power law in a large temperature interval, presumably these materials are near the metal-insulator transition which happens at the critical interchain coupling. Poorly conducting samples with σ_{RT} of the order of or less than 1 S/cm demonstrate a behavior that can be classified as dielectric [4]: It is similar to that observed in amorphous semiconductors. Namely, dc conductivity is strongly dependent on temperature and its best fit is given by a "1D Mott's law": $\Sigma_{\mathrm{dc}} \propto \exp -(T_0/T)^{1/2}$. For a variable range hopping mechanism of transport, the temperature dependence of conductivity is [5,6] $\Sigma_{\mathrm{dc}} \propto \exp -(T_0/T)^{1/(d+1)}$, where $d > 1$ is the system's dimension. This is not true, however, in a 1D case [7], for which it should be the Arhenius dependence, $\Sigma_{\mathrm{dc}} \propto \exp -(T_0/T)$.

Experimental measurements of the microwave conductivity and the dielectric constant of these poorly conducting samples [4,8] revealed that both are strongly dependent upon temperature too, most probably according to the same 1D Mott's law. The theory of hopping transport predicts, however, only a very weak power temperature dependence for the frequency-dependent conductivity and the dielectric constant in two- and three-dimensional systems [9].

In the present Letter we suggest an explanation for these peculiar features of conducting polymers that is based on the specific structure of the polymer network. In the stretched polyacetylene, this network is formed by coupled polymer chains oriented along some direction. Electronic micrographs show that in these substances polymeric chains are organized into *fibrils* [1], which may be distinctly seen to be subdivided into smaller ones [10]. In a nonfibrillar form of conducting polymers, like polyaniline, x-ray data reveal the existence of highly ordered "crystallinity regions" with metallic properties [1]. Therefore the whole network in the stretched polyaniline may be thought of as constructed from long one-dimensional polymer chains randomly coupled by metallic crystallinity islands of various sizes. The volume fraction of later ones can be small.

We assume here that a polymer structure represents a *nearly one-dimensional fractal*. That means a specific kind of polymer chain organization, defined in the following way: Choose a three-dimensional cube with the edge L. Chains, which are coupled within this cube, form a set of bundles disconnected from each other. If for large enough L the cross section of the maximum bundle is proportional to L^{ϵ}, where $0 \le \epsilon \le 2$, then we shall call the system $d^* = (1 + \epsilon)$ dimensional. Obviously, $\epsilon = 0$ for purely one-dimensional systems (sets of uncoupled chains). Note that if one assumes chains to be connected either with low concentration of uncorrelated interchain links, or with weak links (their resistivities being high compared to intrachain ones in our example), then we are dealing with a *quasi-one-dimensional* system [3], which is three dimensional according to our definition.

The transport mechanism in conducting polymers in the localized phase is assumed to be the variable range hopping type (VRH) [11]. The regular method to treat VRH models is the effective medium approximation [9], which gives wrong results in the nearly 1D case. For example, for the percolation model it gives a threshold concentration of broken bonds $c_t \approx \epsilon$, while $c_t \approx \exp(-1/\epsilon)$, as we shall see later. The results for the critical exponents are also wrong in this case. We choose the following approach.

We will first study the nearly 1D percolation system exactly. The VRH model is reduced to the percolation problem by constructing the effective percolation lattice [6,9].

Our first aim is the study of the critical behavior of the conductivity near the percolation threshold in a d-dimensional lattice, where d is close to the lower critical dimensionality, i.e., $d = 1 + \epsilon$, $\epsilon \ll 1$. The real space renormalization group of Migdal and Kadanoff (RGMK) [12–14], that is exact at $d = 1$, is expected to be the appropriate tool if d is close to 1. This method was applied to the percolation conductivity problem by Kirkpatrick [15], but the case of dimensionality close to 1 did not get any special attention.

The RGMK method may be formulated as follows: The d-dimensional hypercubic lattice is replaced by a (m, n) hierarchical structure (see below) with $m = n^{d-1}$, and $n \to 1$ afterwards. The (m, n) hierarchical pseudolattice may be constructed by the infinite repetition of two subsequent steps, as illustrated in Fig. 1: (a) formation of an n-length chain from n bonds, (b) formation of an m bundle with m chains in a cross section. Bundles obtained in this way are used as elementary bonds at the next stage, etc. To have a continuous RG transformation instead of a discrete transformation, one should proceed to infinitesimal transformation, setting $n = 1 + \nu$, $m = 1 + \epsilon\nu$; $\nu \to 0$, where $\epsilon = d - 1$. At this step we introduce the continuous scale variable $\lambda = \exp(\nu l)$, where l is the order of bonds in the hierarchical structure.

It appears to be convenient to work with conductivity Σ and resistivity $R = 1/\Sigma$ distribution functions in the Laplace representation:

$$P(\sigma) \equiv \langle \exp(-\sigma\Sigma)\rangle; \quad Q(s) \equiv \langle \exp(-sR)\rangle . \tag{1}$$

This is justified by the fact that for the chains or the bundles formation we have simply sums of independent random resistivities or conductivities, respectively. These functions are related by the following integral transformation:

$$P(\sigma) = 1 - \sqrt{\sigma} \int_0^\infty \frac{ds}{\sqrt{s}} J_1(2\sqrt{s\sigma})Q(s) , \tag{2}$$

where $J_1(s)$ is the Bessel function. For the hierarchical structures, we arrive, after the transition to a continuous transformation, at the following equation:

$$\lambda \frac{\partial Q(s,\lambda)}{\partial \lambda} + (1 - \epsilon)\frac{\partial Q(s,\lambda)}{\partial s} - Q(s,\lambda)\ln Q(s,\lambda) + \epsilon\sqrt{s}\int_0^\infty \frac{d\sigma}{\sqrt{\sigma}} \times J_1(2\sqrt{s\sigma})P(\sigma,\lambda)\ln P(\sigma,\lambda) = 0 . \tag{3}$$

Finite concentration of broken bonds c_b may be considered by introducing the boundary conditions

$$Q(s,\lambda)|_{s=0} = 1 - c_b \Longleftrightarrow P(\sigma,\lambda)|_{\sigma=+\infty} = c_b . \tag{4}$$

Setting in Eq. (3) $s \to 0$, we obtain the RGMK equations for broken bond concentration,

$$\lambda \frac{dc_b}{d\lambda} = \epsilon c_b \ln c_b - (1 - c_b)\ln(1 - c_b) . \tag{5}$$

There are three fixed points, two stable ones, $c_b = 0$ (regular lattice) and $c_b = 1$ (completely broken lattice), and one unstable fixed point $c_b = c_t$, where the threshold concentration c_t $(0 < c_t < 1)$ is given by

$$\epsilon c_t \ln c_t = (1 - c_t)\ln(1 - c_t) . \tag{6}$$

At arbitrary values of ϵ one can solve Eq. (3) only numerically. Numerical results concerning this solution under the threshold boundary conditions, $Q|_{s=0} = 1 - c_t$, $Q|_{s=+\infty} = 0$, support the following assertion: The function $Q(s,\lambda)$ eventually evolves at sufficiently large λ into the following automodeling form:

$$Q(s,\lambda) = \overline{Q}(s\lambda^a), \qquad P(\sigma,\lambda) = \overline{P}(\sigma\lambda^{-a}) , \tag{7}$$

where a is the ϵ-dependent exponent. This form ensures, together with Eq. (5), the power-law critical behavior of the conductivity Σ:

$$\Sigma(\tau) \sim \tau^t, \qquad \tau = c - c_t/c_t , \qquad t = a\nu . \tag{8}$$

Here ν is the critical exponent of the correlation length (the characteristic size of a finite connected cluster) that is determined from Eq. (5) by linearizing near the threshold point:

$$\nu^{-1} = \epsilon(\ln c_t + 1) + 1 + \ln(1 - c_t) , \tag{9}$$

where c_t is given by Eq. (6). The critical index for the conductivity t as a function of ϵ can be found only numerically, and the result is shown in Fig. 2.

In the limit of small ϵ the problem may be treated analytically. In this case the threshold concentration and the critical index of the correlation length are given by

$$c_t = e^{-1/\epsilon}, \quad \nu^{-1} = \epsilon - \tfrac{1}{2}e^{-1/\epsilon} + \cdots . \tag{10}$$

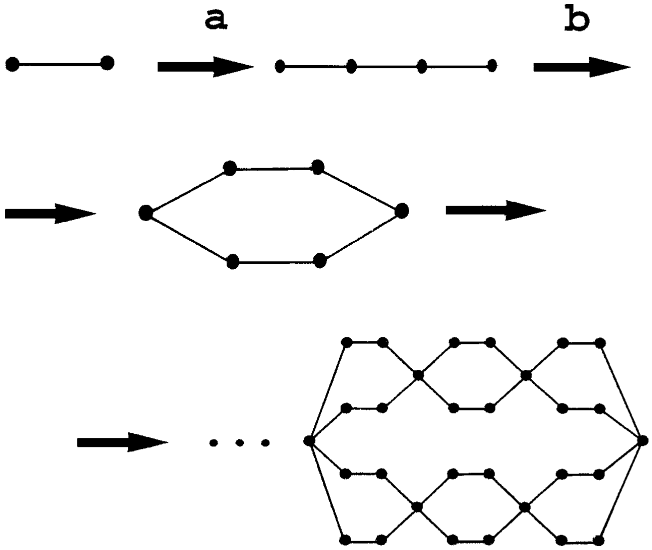

FIG. 1. The two initial stages of $(2, 3)$ hierarchical structure formation.

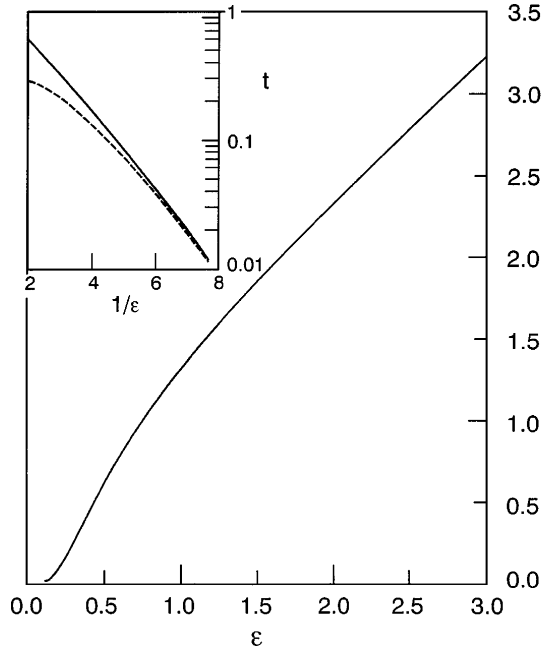

FIG. 2. The conductivity exponent t as a function of $\epsilon = d - 1$. The inset shows the comparison of numerical (solid curve) and analytical results.

One can see that although the main part of $\nu^{-1}(\epsilon)$ dependence is linear, the remaining dependence on ϵ is essentially nonanalytic, and therefore no regular ϵ expansion in $(1 + \epsilon)$ dimensions is possible.

Let us look for the automodeling solution (7) at $\epsilon \ll 1$. Using the fact that for $\epsilon = 0$ this solution is simply $\exp(-s)$ $(a = 0)$, we assume

$$\overline{Q}(x) = (1 - c_t)\exp[-x + v(x)], \qquad (11)$$

as well as $a \sim c_t$, $v \sim c_t$. Plugging Eqs. (7), (10), and (11) into Eq. (3), linearizing in v, and neglecting higher-order terms over c_t, such as av, c_t^2, $c_t v$, etc., we arrive at the following equation:

$$\xi v'' - \xi v' + v = e^{-1/\epsilon}\left[1 - \frac{J_1(2\sqrt{\xi})}{\sqrt{\xi}} \times \exp\left(\frac{\epsilon\xi}{1 + \epsilon}\right)\right] - a\epsilon\xi\,, \qquad (12)$$

where $x = \epsilon\xi/(1 + \epsilon)$.

The solution of Eq. (12) with $v(0) = v'(0) = 0$ can be found by the substitution $v(\xi) = \xi w(\xi)$. We have

$$w'(\xi) = \frac{e^{\xi}}{\xi^2}\left[e^{-1/\epsilon}\left(1 - e^{-\xi} - \int_0^{\xi} \frac{d\eta}{\sqrt{\eta}}\, e^{-\eta/(1+\epsilon)} J_1(2\sqrt{\eta})\right) - \epsilon a[1 - (1 + \xi)e^{-\xi}]\right]. \qquad (13)$$

To eliminate here the term, growing at $\xi \gg 1$ as $\exp\xi \simeq \exp(x/\epsilon)$, the following condition should be fulfilled:

$$\epsilon a = c_t\left(1 - \int_0^{\infty} \frac{d\eta}{\sqrt{\eta}}\, e^{-\eta/(1+\epsilon)} J_1(2\sqrt{\eta})\right). \qquad (14)$$

This equation determines the critical exponent for the conductivity $t = a\nu$ [see Eq. (8)]. By combining Eqs. (10) and (14) we get

$$t = \epsilon^{-2}\exp(-1 - 1/\epsilon)\,. \qquad (15)$$

The coefficients v_n of a Tailor expansion of $v(x)$ at $x = 0$ represent the cumulants of the distribution function for resistivities, e.g., $v_2 = (\langle R^2\rangle - \langle R\rangle^2)/\langle R\rangle^2$. They are obviously of the order of c_t. That means that the resistivity distribution at length scale λ is of an almost Gaussian δ function, centered at $\langle R\rangle \propto \lambda^a$ and with the width $\propto \lambda^a \exp(-1/\epsilon)$.

Using the scaling arguments [16,17], one can derive the low-frequency part of the ac conductivity $\Sigma(\omega, \tau)$ near the percolation threshold, if the critical exponent of the dc conductivity is known. System conductivity at low frequencies $\omega \ll W_0$ (W_0 is the hopping rate of the retaining bonds) and near the percolation threshold $\tau \ll 1$ is supposed to be represented in the scaling form

$$\Sigma(\omega, \tau) = \frac{e^2 n_e}{kT} a_{\|}^2 |\tau|^t W_0 g\left[\tau\left(\frac{S}{W_0}\right)^{-u/t}\right], \qquad (16)$$

where $S = -i\omega$, $a_{\|}$ is the longitudinal lattice constant,

$$u = t/(s + t), \quad s = 2\nu - \beta\,. \qquad (17)$$

Here s and u represent the critical exponents for the dielectric constant near the percolation threshold and the frequency-dependent conductivity at the threshold, respectively, and β is the exponent of the percolation order parameter (the probability of the site to belong to the infinite cluster). The scaling function $g(x)$ has the following asymptotic behavior:

$$g(x) \approx \begin{cases} A|x|^{-t}, \text{ as } |x| \ll 1\,, \\ 1 + B_+ x^{-s-t} + \ldots, \text{ as } x \gg 1\,, \\ B_-|x|^{-s-t} + \ldots, \text{ as } x < 0, \quad |x| \gg 1\,. \end{cases}$$

The critical exponent β in nearly one-dimensional systems is very small, $B = c_t^2/(3\epsilon)$ and hence $s \approx 2\nu$.

Now let us consider a nearly one-dimensional system with variable range hopping along the chains. We assume [5] that the hopping rates depend on the intersite distances $r_{ij} = |r_i - r_j|$ and on the energy difference $\varepsilon_{ij} = |\varepsilon_i - \varepsilon_j|$ via $f_{ij} = r_{ij}/a + \varepsilon_{ij}/2kT$ (a is the localization radius) as $W_{ij} = \omega_0 \exp(-2f_{ij})$. Assuming site positions and energies near the Fermi level homogeneously distributed with the density N_F, we arrive at the "two-dimensional Poisson" distribution for f_{ij}, $F(f) = \exp[-(f/f_0)^2]$, with $f_0 = (T_0/T)^{1/2}$, $kT_0 = (N_F a)^{-1}$.

It is known [9] that the behavior of the conductivity with continuously distributed hopping rates may be explained, at least qualitatively, if the result for the percolation lattice is known. For this purpose, we choose some trial value of the hopping rates W_c. Then the initial system is replaced by the percolation network where the hopping rates less than W_c are set to zero (broken bonds) and all others are set equal to W_c. The conductivity of such a system is obviously less than the initial one. If the trial value of W_c is chosen so that the conductivity of the percolation system is maximal, one can hope that this value gives a good estimate for the conductivity of the real system.

Performing this procedure, e.g., at zero frequency, one can find that the dc conductivity is determined by the hops with f_{ij} very close to its threshold value f_t, which is determined by $F(f_t) = c_t$. From Eq. (10) it follows that $f_t = f_0/\sqrt{\epsilon} = (T_1/T)^{1/2}$, where $T_1 = T_0/\epsilon = (\epsilon N_F a)^{-1}$. Taking in Eq. (16) $n_e = N_F kT$ and $a_{\|} = 1/n_e$, we have

$$\Sigma_{\mathrm{dc}} = \frac{e^2 W_t}{N_F (kT)^2} = \frac{e^2 \omega_0}{N_F (kT)^2} \exp[-(T_1/T)^{1/2}]. \quad (18)$$

At the lowest frequencies (hydrodynamical region, $\omega \ll \omega_h$) the conductivity can be close to its dc value and may be represented as a power series in $-i\omega$: $\Sigma[\omega] = \Sigma_{\mathrm{dc}}(1 - i\omega/\omega_h - \cdots)$, with a very small value for ω_h. As a result, the static dielectric constant η becomes very large and strongly temperature dependent:

$$\eta \sim W_t/\omega_h \sim (T_1/T)^{1/\epsilon} \exp(2/\epsilon^2). \quad (19)$$

At $\omega \gg \omega_h$ the frequency dependence of conductivity is given by

$$\Sigma(\omega) = \frac{e^2 W_t}{N_F (kT)^2} \exp\left[\epsilon \left(\frac{T_1}{T}\right)^{1/2} \left(\frac{-i\omega}{W_t}\right)^{\epsilon/2}\right]. \quad (20)$$

Here the temperature dependencies of the conductivity and of the dielectric constant remain essentially of the 1D Mott's type. If the temperature is relatively high, i.e., $T \gg T_2$ ($T_2 = \epsilon^4 T_1/4$), this dependence would continuously turn into one that is typical for $d = 1$ (see, e.g., [3]) at frequencies of the order of ω_m, $\ln(\omega_m/W_t) \sim -2/\epsilon$. At lower temperatures, $T \ll T_2$, Eq. (20) is valid only until $\omega \ll \tilde{\omega}_m$, $\ln(\tilde{\omega}_m/W_t) \sim -(1/\epsilon)\ln(T_2/T)$. At $\tilde{\omega}_m \ll \omega \ll \omega_M$, where $\ln(\omega_M/\tilde{\omega}_m) \sim \epsilon(T_1/T)^{1/2}$, we have the following dependence:

$$\Sigma(\omega) = \frac{e^2}{N_F (kT)^2} (-i\omega) \left[\frac{\epsilon (T_1/T)^{1/2}}{\ln(-i\omega/\tilde{\omega}_m)}\right]^2, \quad (21)$$

which changes into a one-dimensional one (some power of temperature) at $\omega \sim \omega_M$.

In sum, by taking into account the specific fractal structure of polymer networks we obtained a very specific temperature dependence for the static conductivity [Eq. (18)], dielectric constant [Eq. (19)], and frequency-dependent conductivity [Eqs. (20),(21)]. The source of this dependence is the following. The low-dimensional random system can be separated in weakly coupled clusters within which carriers occur to be locked. With temperature, the size of clusters exponentially increases, since more space becomes accessible for carriers due to thermal activation. As a result, the dielectric constant and the conductivity exhibit strong temperature dependencies. There is also the very strong frequency dispersion of conductivity starting with extremely low frequencies. Such a type of strong temperature and frequency dependence is actually observed in conducting polymers with localized carriers [4,8].

Let us stress again that a similar dependence cannot be obtained within the standard 2D or 3D hopping models. By assuming the strong Coulomb repulsion between carriers, the 1D Mott's law could be reproduced [6], but it does not lead to any strong dependence for the dielectric constant and for the frequency-dependent conductivity. The reason is the following. In contrast to the low-dimensional case, the clusters in 2D and 3D systems prove to be more effectively coupled. Therefore the large polarization of clusters does not happen because of leakage of carriers. Thus our results support strongly the idea that the conducting polymers represent a low-dimensional substance even in the dielectric phase.

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