# Localization Transition in a Random Network of Metallic Wires: A Model for Highly Conducting Polymers

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We consider the Anderson metal-insulator transition in a network of randomly coupled metallic wires, which is suggested to describe transport properties of highly conducting fibril-form polymers. The absence of closed paths in the model enables us to study the transition exactly. The critical concentration of the cross-links determining the transition depends on the localization length of a single wire and on the interwire coupling. Application of a magnetic field extends the area of the metallic phase.

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Recently, conjugated polymers such as polyacetylene, polyaniline, and polypyrrole have attracted considerable interest in applied and fundamental research [1,2]. Their common exciting feature is that the conductivity can be increased by a few orders of magnitude upon doping. In heavily doped Tsukamoto polyacetylene the room-temperature conductivity ($\sigma_{RT}$) has already reached that of Cu. However, in spite of the large $\sigma_{RT}$, transport properties of these conducting polymers are still far from being traditionally metallic.

First of all, in contrast to metals, the conductivity of the polymers decreases with lowering the temperature. Depending on $\sigma_{RT}$ (i.e., on the level of doping and the degree of disorder) this decay varies from an activation-type behavior to a weak logarithmic one. For the most highly conducting samples the conductivity even approaches a residual value at low temperatures [2–4]. At the same time their thermoelectric power and Pauli susceptibility suggest a metallic density of states at the Fermi level in the whole temperature interval. It is noteworthy also that at low temperatures there is a significant magnetoresistance [3,4] and its sign correlates with the above temperature dependence of conductivity, being negative for highly conducting samples.

On the basis of these observations it was suggested [3–6] that the highly conducting polymers are close to a metal-insulator (MI) transition driven by disorder. Since their $\sigma_{RT}$ greatly exceeds those of all known systems near the MI boundary, one can conclude also that the highly conducting polymers exhibit a new type of localization-delocalization transition.

For a physical explanation of the unusual transport properties of the polymers their chain nature seems to be very important. Electrons move primarily along polymer chains over large distances without scattering, hopping sometimes between neighboring chains. Therefore, existing theoretical considerations were based on models of either highly anisotropic dirty metals [4,7], or a quasi-one-dimensional system of weakly coupled chains [3,8]. The direct application of these results to polyacetylene requires a very high anisotropy of the conductivities [4,9]. However, this basic assumption of high anisotropy, based on a regular arrangement of chains, is violated in the polymers.

It is common knowledge that the polymers represent a very irregular structure of interacting chains, whose description and classification are a subject of current studies [10]. The most well-known polymer, polyacetylene [1], has a so-called fibril structure: single chains are coupled into fibrils which occupy a part of the whole volume. The fibrils are bent in the space in a very complicated way. They come in contact with each other forming a random cross-linked network. The fibril structure is schematically illustrated in Fig. 1.

At first glance the "spaghetti" morphology makes the evaluation of the transport properties for the polymers practically untractable and until now their quantitative description has not been attempted. In this Letter we present for the first time an original model for the study of the kinetics in such irregular structures. To define our model we assume that each fibril is a weakly disordered metallic wire and that the cross-links between the fibrils can be described by interwire junctions. As a result, we have a network of randomly coupled metallic wires.

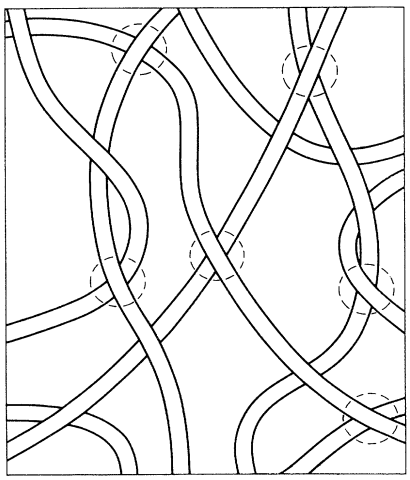

FIG. 1. Schematic view of the fibril structure of polymer. The rings indicate the interfibril cross-links.

In the absence of the junctions all the electronic states of the wires are localized by any weak disorder [11,12]. The states become extended over the whole network only for strong enough interwire electron transfers. Within the present model we determine the position of the MI transition and the critical behavior as a function of the intrinsic disorder and of the interwire coupling.

We would like to emphasize that the existence of the delocalized phase in the network is a nontrivial phenomenon. Indeed, due to its irregularity, the random network should be considered as strongly disordered, and therefore all the electronic states might remain localized. However, it is not so and we prove the existence of the MI transition in the network. Whether the electronic states are localized or extended emerges only in the low-temperature conductivity. At high temperatures, due to inelastic scattering, electrons are delocalized, and the network always demonstrates a metallic conductivity even in the absence of cross-links. This property of our model can, in principle, reconcile the observable controversy between the high- and low-temperature conductivities of the polymers. One can also note that the thermodynamic characteristics of the network always correspond to a metallic density of states at the Fermi level in both the metallic and dielectric phases.

Let us start with specifying the model. Two apparent spatial parameters can be introduced to characterize the network: the concentration of the junctions per unit length along the wire, $p$, and the concentration of the wires per unit area, $n_2$. The ratio $n_2/p^2$ plays the role of the mean number of "neighbors" in the network. Indeed, a segment of a wire of length $1/p$ is surrounded by approximately $n_2/p^2$ other wires, one of which the wire contacts over this length. We assume that

$$n_2/p^2 \gg 1 \tag{1}$$

and then, like in the theory of phase transitions, the mean field approximation with respect to the interwire coupling becomes exact. In other words, due to the inequality (1) the statistical weight of the closed paths, consisting of a few wires, is additionally reduced for the present network in comparison with the corresponding regular lattice.

The wires of the network are well specified by the density of states at the Fermi level per unit of wire length, $\tilde{\nu}$, and the Drude diffusion coefficient along the wire, $D_0$. In terms of these parameters the localization length $R_0$ for the states of the wire is equal to [11,12]

$$R_0 = 2\pi\hbar\tilde{\nu}D_0 \ . \tag{2}$$

The description in terms of $\tilde{\nu}$ and $D_0$ holds for the fibrils, provided the interchain transfer integral $t_\perp$ within the fibril is restricted to the region [12]

$$\hbar/\tau \ll t_\perp \ll M\hbar/\tau \, , \tag{3}$$

where $M$ is the number of chains in the fibril. Equation (3) ensures that the chains are coupled strongly enough and

$$R_0 = 2Ml \, , \tag{4}$$

where $l$ is the mean free path along the chain.

We describe junctions between the wires by pointlike contacts with the amplitude of electron-transfer integral $\tilde{J}$. The dimensionless parameter, characterizing the intensity the interwire transitions at the contact, is the Born cross section of "capture" by the contact

$$\alpha = (\pi\tilde{J}\tilde{\nu})^2 \ . \tag{5}$$

We assume that the contacts are randomly distributed over the wires with a low linear concentration $p$ such that the following inequality holds:

$$l_J \gg l \ , \quad l_J \simeq \max(1/p, 1/\alpha p) \, , \tag{6}$$

where $l_J$ is the characteristic length of scattering by the junctions. In this case the localization is mainly caused by the intrawire scattering and a contribution of a disorder due to the random cross-links to the localization is negligible. The principal effect of switching cross-links is the extension of the localized wave functions over an increasingly large number of the wires. Therefore the delocalization transition is expected at some critical concentration $p_c$, which is for thick enough wires ($R_0 \gg l$) in the region (6).

The above two types of disorder in the system should be essentially distinguished. The first is the weak intrawire disorder due to intrinsic impurities, and the second one is related to the random distribution of interwire contacts over the network. As concerns the first one we can independently average over the impurity potential of the wires by using the supersymmetry method [11]. As a result we find that the dynamic correlations at a frequency $\omega$ in the given network are described by a supersymmetric $\sigma$ model. The free energy functional of the $j$-th wire is ($\hbar = 1$)

$$F[Q_j] = \frac{\pi\tilde{\nu}}{8}\int dx \, \mathrm{Str}[D_0(\nabla Q_j)^2 + 2i\,\omega\Lambda Q_j] \ , \tag{7}$$

where Str stands for the supertrace introduced in Ref. [11], and $Q$ is the supermatrix such as $Q^2 = 1$ and $\Lambda^{11} = -\Lambda^{22} = 1$. The notations for the elements in Eq. (7) are the same as in Ref. [11]. The electron hops between wires $i$ and $j$ are included in the total functional with the Josephson-type terms

$$\Delta F[Q_i, Q_j] = \frac{\alpha}{8}\,\mathrm{Str}[Q_i(x_i) - Q_j(x_j)]^2 \ , \tag{8}$$

where $x_i$ and $x_j$ are the cross-link coordinates along the $i$-th and $j$-th wires. In terms of $Q$-matrix elements the density-density correlation function for the $j$-th wire of the network considered reads

$$K_j(x,\omega) = -2(\pi\tilde{\nu})^2 \int Q_{j,\alpha\beta}(0)Q_{j,\alpha\beta}(x) \times \exp(-F[Q]) \prod_i DQ_i(y) \ , \tag{9}$$

where the functional integration over $Q$ is implied. The observable one-wire correlator can be obtained from Eq. (9) after averaging $K_j(x,\omega)$ over all realizations of the random network:

$$K(x,\omega) = \langle K_j(x,\omega)\rangle_\alpha . \quad (10)$$

Although being somewhat technically complicated the supersymmetry approach is the only reliable one to describe the MI transition in the model under consideration. We outline the basic steps of the evaluation of Eqs. (7)–(10). The absence of the closed paths in the network allows us to use the transfer-matrix method for evaluating the functional integral (9). Within this method the expansion along the interwire couplings arises in a natural way, and then the averaging over the random junction positions (the second type of disorder) can be straightforwardly carried out. As a result the problem is finally reduced to the solution of integro-differential equations. The equations are similar to those obtained for a model on the Bethe lattice in Refs. [13–15], and therefore their analysis can be done in the same way. Let us first present the final results for the case of strong magnetic fields.

At low concentrations of the cross-links the dielectric phase persists and the one-wire correlator (10) decays exponentially at large distances with the localization length $R_{\rm loc}$ corresponding to uncoupled wires

$$K(x,\omega\to 0) = \frac{1}{-i\omega}\exp\left[-\frac{x}{2R_{\rm loc}}\right], \quad R_{\rm loc} = 2R_0. \quad (11)$$

The doubling of the localization length in Eq. (11) is due to the strong magnetic field.

If the concentration of links is large enough the dielectric $1/\omega$ asymptotic (11) is no longer valid and the conducting regime realizes. The critical concentration of the MI transition, $p = p_c(\alpha)$, is given by the equation

$$[4\alpha p_c(\alpha)R_{\rm loc}]^{-1} = K_0(\alpha)\left(\vec{\partial}_\alpha - \overleftarrow{\partial}_\alpha\right) I_{1/2}(\alpha) , \quad (12)$$

where $K_0(\alpha)$ and $I_{1/2}(\alpha)$ are the Bessel functions. The MI boundary obtained from Eq. (12) is shown in Fig. 2.

We would like to draw attention to the weak dependence $p_c(\alpha)$ at not too small $\alpha$. At $\alpha \gg 1$, $p_c(\alpha)$ approaches a constant

$$p_c = 1/4R_{\rm loc} . \quad (13)$$

This result can be interpreted in the following way. The strong interwire coupling leads to the appearance of mixed states located on two interacting wires. The energy of these states is randomly spread around the Fermi level within $\Delta E = \omega_0$, where

$$\omega_0 = 4D_0/R_{\rm loc}^2 . \quad (14)$$

Being near the links these states are randomly distributed also over the network. The typical overlap between them equals $\delta E = \omega_0 \exp[-2/(pR_{\rm loc})]$, because of the exponential localization of states within wire. According to the arguments of Thouless [16], the MI transition occurs at $\delta E \approx \Delta E$, i.e., at $p_c R_{\rm loc} \approx 1$, which is in agreement with Eq. (13).

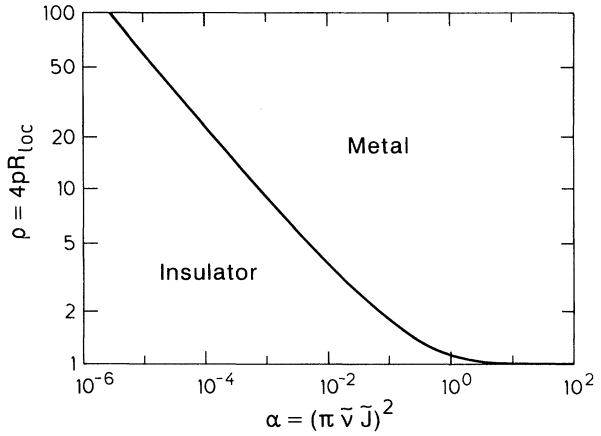


FIG. 2. Phase diagram of the random metallic network.

For weak coupling, $\alpha \ll 1$, we obtain from Eq. (12)

$$p_c = (1/4R_{\rm loc})\,(2\pi/\alpha)^{1/2}\,[2 - C + \ln(2/\alpha)]^{-1} , \quad (15)$$

where $C = 0.577$ is Euler's constant. Equation (15) can be approximately rewritten as $p_c R_{\rm loc} \approx 1/\sqrt{\alpha}$. The product $pR_{\rm loc}$ gives the number $m \gg 1$ of the states, with which the given localized state interacts. On the other hand the dimensionless parameter of the interwire coupling can also be represented for the localized states as $\alpha \approx (J/\Delta)^2 \ll 1$, where $J$ is the overlap integral and $\Delta$ is the energy spacing between the localized states. Thus, the critical concentration of the links $p_c$ corresponds again to the case when the energy separation between the interacting states $\Delta/m$ becomes comparable with their overlap $J$. This transition resembles for weak coupling the MI transition on the Bethe lattice [13–15] with the coordination number $m \gg 1$.

The behavior (11) is valid in the whole region of the dielectric phase, including also the critical point. It is a characteristic feature of the dielectric phase in the network that the localization length along the wire is insensitive to interwire coupling. On the metallic side near the transition the correlator can be found to be

$$K(x,\omega\to 0) = \exp[-2\pi/\delta - x/2R_{\rm loc}] , \quad (16)$$

where $\delta^2 = [p/p_c(\alpha) - 1] \ll 1$ . The dynamics of spreading the electron over the wires is more explicitly described by the function $P(\omega) = \int dx K(x,\omega)$, for which one can write the representation

$$P(\omega\to 0) = [-i\omega + W]^{-1} . \quad (17)$$

Here $W$ is the frequency of the interwire hopping and correspondingly $W^{-1}$ is the lifetime of the electron within the wire. From Eqs. (16) and (17) one can see that $W$ decreases abruptly when approaching the critical point

$$W = W_0 \exp[-2\pi/\delta] . \quad (18)$$

In the deeply metallic region, $p \gg p_c(\alpha)$, the correlator (10) acquires a diffusive form

$$K(q,\omega) = [-i\omega + D_0 q^2 + W_0]^{-1} , \quad (19)$$

which remains valid as long as $\omega$ or $W_0$ is larger than $\omega_0$, Eq. (14). At $\alpha \gg 1$, $W_0$ is the inverse mean time of the classical diffusion between the neighboring links, $W_0 = p^2 D_0$. The condition $W_0 \gg \omega_0$ is analogous to the requirement $p \gg p_c \approx 1/R_{\rm loc}$. In the limit of weak coupling, $\alpha \ll 1$, one can obtain the expression $W_0 = \pi\tilde{\nu}\tilde{J}^2 p$, which holds at least at $pR_{\rm loc} \gg 1/\alpha$.

Until now we considered the case of strong magnetic fields. All calculations can also be repeated in the absence of magnetic fields [11,13]. The difference between these two cases is finally reduced to the change of the localization length in (11)–(16) which in the limit of weak and strong magnetic fields equals

$$R_{\rm loc}(H=0) = R_0 \ , \quad R_{\rm loc}(H=\infty) = 2R_0 \ . \tag{20}$$

Using Eqs. (13), (15), and (20) one can see that the magnetic field shifts the transition to a lower concentration of the cross-links. Due to a random orientation of wires with respect to the field direction the region of the crossover between these two limits is very broad,

$$H_c = (\hbar c/e\sqrt{S})\left(1/R_0 \div 1/\sqrt{S}\right) , \tag{21}$$

where $S \ll R_0^2$ is the cross section of the wire.

Although when deriving the phase diagram (Fig. 2) we used the inequality (1) which enables us to neglect closed paths, we believe that the phase diagram remains qualitatively correct for the whole region of parameters. For example, at weak coupling $\alpha \ll 1$, this case often being realized in real polymers, Eq. (15) for the critical concentration can be represented in the form

$$\tilde{J}p_c \approx \omega_0 \, . \tag{22}$$

In an application to more compact oriented polymers such as Durham-Graz polyacetylene, where the concentration of links $p$ is expected to be high, the product $\tilde{J}p$ plays the role of an effective bandwidth in the transverse direction with respect to the axis of stretching. Equation (22) shows that the transition occurs when this bandwidth becomes comparable with the energy spacing $\omega_0$ between localized states. This conclusion looks reasonable and is in agreement with a quasi-1D consideration in Ref. [8].

A MI transition in the intrafibril disorder produced by aging is observed in the heavily doped polyacetylene and polypyrrole [6]. In our model such a disorder is incorporated into $R_{\rm loc}$. Being inversely proportional to the concentration of the internal defects, $R_{\rm loc}$ decreases with disorder, and at the critical disorder determined by Eq. (12) the system becomes macroscopically dielectric. Note that according to the phase diagram in Fig. 2 the conducting state is more sensitive to the value $pR_{\rm loc}$ than to the strength of the interwire coupling $\alpha$ and, therefore, can be more easily induced by an increase of $pR_{\rm loc}$. Experimentally this tendency is seen in the appreciable enhancement of the low-temperature conductivity without signs of saturation under application of the magnetic field [3,4], pressure [17], and stretching [18,19]. The fact that the conductivity is controlled by the cross-linkings was most explicitly demonstrated in Ref. [10] for polyaniline.

In summary, we suggested a new model for the description of electronic properties in fibril-form polymers with a completely irregular structure. The MI transition studied within this model enables us to understand peculiarities of transport in the novel highly conducting polymers.

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