

Delocalization in Weakly Coupled Disordered Wires: Application to Conjugated Polymers

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It is well known that even for minimal disorder one-dimensional wires are insulators: all 1D electron states are localized. Here, the influence of interwire coupling on delocalization of 1D states is examined. Based on perturbation theoretic arguments for the formation of 3D states in coupled wires and subsequent scaling analysis, practical expressions for the microscopic conditions of electronic delocalization and coherent conductivity of coupled 1D wires are obtained. The model quantitatively explains the temperature dependent dc conductivity in conducting polymers at both sides of the metal-insulator transition and links the experimental data to microscopic material parameters.

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The scaling theory of Anderson localization [1] has shaped our understanding of disordered systems. Above a critical level of disorder, constructive interference of multiply backscattered carrier waves leads to a permanent occupation probability at the initial site: the state is localized. For dimension $d = 1$, repeated scattering always leads to localization as all trajectories self-interfere. The quantum coherent resistance of a one-dimensional wire of length L grows exponentially with L/ζ . The localization length ζ decreases with growing disorder. In practical cases, a physical ensemble of 1D conductors always exhibits interwire coupling I_{\perp} , suppressing localization. Eventually, a transition from 1D to 3D behavior occurs as demonstrated by computer simulations [2]. Interesting examples are conducting polymers like polypyrrole (PPy), polyacetylene (PAC), poly(*p*-phenylene vinylene) (PPV), and ropes or mats of single-wall carbon nanotubes (SWNT), where, despite disorder and the 1D structure, a “metallic” phase (macroscopically conducting at temperature $T = 0$) may be formed [3–8]. Such systems can neither be considered as purely 1D nor as purely 3D systems and hence fall beyond the scope of the conventional scaling theory of localization. As a result, our understanding remains incomplete and the central question “which microscopic conditions are required to develop a coherent metallic state in disordered quasi-1D systems?” is yet unanswered.

The purpose of this Letter is to elucidate this question. Starting point is a microscopic model of disordered wires where the coupling is treated as a perturbation of the 1D states. The final outcome is that for

$$\frac{2I_{\perp}}{\Delta} \frac{\zeta}{a} \sqrt{\frac{a \ln(\zeta/ag_c)}{\zeta}} > 1, \quad (1)$$

a metallic state is present in a system of coupled 1D wires. Here, I_{\perp} is the interchain transfer integral, Δ the 1D level splitting, ζ the intrachain localization length, and a the intrachain lattice constant. The constant $g_c = 1/\pi^2$ [1] is the critical dimensionless conductance demarking the metal-to-insulator transition in scaling theory. Equation (1) can be understood as follows. The first factor on

the left-hand side, $2I_{\perp}/\Delta$, expresses the probability that energy levels of adjacent 1D states, having typical energy separation Δ , both fall within the bandwidth available for interchain transport, $2I_{\perp}$, i.e., the local probability for resonant interwire tunneling. The second factor, ζ/a , counts the number of channels available for interchain transport at the length scale ζ where individual 1D states have appreciable amplitude. The square-root term of order unity is weakly dependent on disorder (ζ/a) and accounts for interference effects. Thus, Eq. (1) estimates the average number of possible resonant interchain tunneling events between 1D states on adjacent chains: delocalization in coupled wires requires on average at least one resonant transition between adjacent wires within the length scale of intrachain localization.

The theory is applied to conducting polymers and SWNT that are tuned through the metal-insulator transition by variation of preparation conditions. Using known microscopic parameters, the model reproduces conductivity data, $\sigma(T)$, in the metallic and insulating phases.

The conductance g of a system of size L^d , which is dimensionless when expressed in terms of the quantum conductance e^2/h , is a direct measure of its disorder. The central idea behind the scaling theory of Anderson localization is that the effective disorder of a system of scale $L + dL$ is fully determined by the value at its previous scale which is quantified by $g(L)$ [1]. The scaling function

$$\beta(g) = d(\ln g)/d(\ln L) = (L/g)(dg/dL) \quad (2)$$

describes this evolution of g with L . For strong disorder all states are localized: $g \ll 1$ decreases exponentially with L : $\beta(g) = \ln(g/g_c) < 0$. For weak disorder scaling is Ohmic: $g \propto L^{d-2}$ and $\beta(g) = d - 2$. Continuity implies that for $d > 2$ a critical conductance g_c exists where $\beta(g)$ changes sign [$g_c = 1/\pi^2$ [1]], which means a crossover from insulating to metallic behavior. In the critical regime $\beta(g) = (g - g_c)/(vg_c)$. The correlation length

$$\xi = L|g(L) - g_c|^{-\nu}, \quad (3)$$

with ν critical conductivity exponent, plays the role as in

other critical phenomena. The macroscopic conductance is obtained by integrating $\beta(g)$ to scales $L \gg \xi$. For $\beta > 0$ the system scales to the metallic phase,

$$g_M(L) = Ag_c(L/\xi), \quad (4)$$

while for $\beta < 0$ the system scales to the insulating phase,

$$g_I(L) = g_c \exp(-BL/\xi), \quad (5)$$

with integration constants $A, B \sim \mathcal{O}(1)$ [1].

For 1D wires, $\beta(g) < 0$ scales always to the localized regime. In case of coupled 1D wires, simulations have shown that a metallic state exists up to a critical level of disorder W_C that decreases as a function of anisotropy [2]. Theoretical studies [9] of \mathcal{N} coupled chains show an increase of localization length up to $\mathcal{N}\zeta$ for strong coupling. Although these studies do point out the influence of interwire coupling on delocalization their results are not easily applied for comparison with data on the experimental systems of interest in this work. Therefore, the goal of the following analysis is to provide a framework for the analysis of conductive properties of a 3D ensemble of nonoriented wires, being a model for, e.g., conducting polymers. First, the conductance at the scale where the system becomes 3D is estimated. Subsequently, scaling according to the β function in 3D is applied to obtain the macroscopic conductivity.

Isolated disordered chains are described by \mathcal{H}_{1D} , including random potential of amplitude W and intrachain charge transfer I_{\parallel} . The system is characterized by eigenstates $|n\rangle$ that are localized with localization length ζ having eigenvalues $\langle n|\mathcal{H}_{1D}|n\rangle$. When spatially close, states have typical energy separation $\Delta_{\zeta} = 1/(N\zeta)$ (N density of states). For weak disorder $W \lesssim I_{\parallel}$, $\Delta \propto W^2$, while $\Delta \propto W$ is expected for strong disorder $W \gg I_{\parallel}$. For coupled chains $\mathcal{H} = \sum_i (\mathcal{H}_{1D,i} + \mathcal{H}_{\perp,i})$, with $\mathcal{H}_{\perp,i} = \sqrt{\epsilon} \sum_{n,m} \langle n|\mathcal{H}'|m\rangle + \text{H.c.}$ and where the summation runs over states m of chain i and states n of adjacent chains. Here $\epsilon \ll 1$ quantifies the interchain mixing probability and \mathcal{H}' being of same order as \mathcal{H}_{1D} describes mixing between neighboring chains. The integrated probability of interchain mixing becomes order unity at length scale

$$\lambda = a/\epsilon \quad (6)$$

(a the microscopic length) and sets the scale where carriers will “sense” the system is 3D and not 1D. One can interpret λ as the length a (free) carrier could travel between successive interchain hops that occur at time scale $a/(\epsilon v_F)$. At this scale \mathcal{H}' operates with typical energy $\langle n|\mathcal{H}'|m\rangle = \Delta_{\lambda} = 1/(N\lambda)$. Using perturbation theory the corrections induced by \mathcal{H}_{\perp} to the unperturbed system \mathcal{H}_{1D} can be estimated. In case of nondegenerate states, the first order correction to the energy levels $\sqrt{\epsilon} \langle n|\mathcal{H}'|n\rangle$ equals zero. Only in second order level shifts become apparent: $\epsilon |\langle n|\mathcal{H}'|m\rangle|^2 / \Delta_{nm} \sim \epsilon \Delta$. The first order correction ψ to the bare $|n\rangle$ is a coherent linear mixture of other 1D wave functions with total amplitude $|\psi|^2 \sim$

$\epsilon |\langle n|\mathcal{H}'|m\rangle / \Delta_{nm}|^2 \sim \epsilon$. For mixing of degenerate states the picture is different. The energy levels are affected already in the first order of perturbation, $\sqrt{\epsilon} \langle n|\mathcal{H}'|m\rangle \sim \sqrt{\epsilon} \Delta$, while the 1D states are mixed already in zeroth order of the perturbation. For both cases ψ extends over multiple chains and reflects a suppression of localization. However, the admixture will produce a truly extended state only if it is composed of infinitely many localized 1D states. This implies that on the scale λ where \mathcal{H}' operates the 1D states should be degenerate to allow full mixing. Because of the uncertainty principle, the finite length scale λ introduces a nonzero width of 1D energy levels [the Thouless energy $E_{c,\lambda} = (1/Na) \exp(-\lambda/\zeta)$]. When $E_{c,\lambda}$ exceeds the average level spacing $\Delta_{\lambda} = 1/N\lambda$ of the localized states living at scale λ , states on adjacent chains are degenerate, which allows resonant transitions.

As a next step, let us derive the interchain conductance g_{\perp} of a microscopic volume $4b^2\lambda$, with b the interchain distance, assuming the above condition holds. The order of magnitude of $g_{\perp} = \epsilon \sum_{n,m} |\langle n|\mathcal{H}'|m\rangle|^2 / \Delta_{nm}^2$ is determined by the smallest denominator Δ_{nm} for which \mathcal{H}'_{nm} is finite; the latter is set by λ . The expectation value $|\mathcal{H}'_{nm}|^2 / \Delta_{nm}^2 \sim 1$ and reflects the resonant nature of transitions. The total conductance can be derived by counting the number of resonant transitions between adjacent chain segments of length λ : the ratio $E_{c,\lambda} / \Delta_{\lambda}$ multiplied by the “filling fraction” ζ/λ to account for the finite extent of the 1D wave functions. This leads to

$$g_{\perp}(\lambda) = \zeta/\lambda \exp(-\lambda/\zeta). \quad (7)$$

In case that $g_{\perp}(\lambda) \gg g_c$, the conductivity $\sigma = (e^2/\hbar) \times (\zeta/4b^2) \exp(-\lambda/\zeta)$ is directly derived. Otherwise, σ should be constructed from a scaling analysis.

At any length scale, the dimensionless conductance g of the system may be calculated from

$$g = \sum_{n,m} |\langle n|\mathcal{H}_{1D} + \sqrt{\epsilon} \mathcal{H}'|m\rangle|^2 / \Delta_{nm}. \quad (8)$$

This expresses the interpretation of conductance as the ratio of the overlap integral of individual states divided by their energy spacing. The expectation values $\langle n|\mathcal{H}_{1D}|m\rangle$ and $\langle n|\sqrt{\epsilon} \mathcal{H}'|m\rangle$ are to be evaluated taking into account the proper effects of boundary conditions at finite length scales. At the smallest length scales, say $\lesssim \zeta$, the conductance is intrinsically anisotropic: along the chain transport is ballistic and $\langle n|\mathcal{H}_{1D}|m\rangle \approx 1$, while perpendicular to the chain $\langle n|\sqrt{\epsilon} \mathcal{H}'|m\rangle \approx \sqrt{\epsilon}$. So conductance perpendicular to the chain is typically a factor ϵ smaller: $g_{\perp}/g_{\parallel} \approx \epsilon$. On the other hand, at macroscopic length scales $\langle n|\mathcal{H}_{1D}|m\rangle = 0$ because of orthogonality of the 1D wave functions, reflecting that transport involving only intrachain transitions scales to zero because of the 1D localization. Hence, at macroscopic length scales, the equation for the conductance simplifies to $g = \epsilon |\langle n|\mathcal{H}'|m\rangle|^2 / \Delta_{nm} \equiv \epsilon g'$. We can exploit this result by performing a scaling analysis for a system that is described

by $\mathcal{H}_{1D} + \mathcal{H}'$ instead of $\mathcal{H}_{1D} + \sqrt{\epsilon}\mathcal{H}'$. Since \mathcal{H}_{1D} and \mathcal{H}' are of the same order of magnitude, the anisotropy of the (microscopic) conductance is eliminated. The corresponding macroscopic conductivity will differ only by a factor ϵ^{-1} from that directly derived from Eq. (8). Hence, multiplying the resulting expression by ϵ the appropriate equation is obtained. This last step could be understood as reflecting an effective carrier density $\propto \epsilon$ involved in interchain transport at any given instant [10].

We thus define the conductance perpendicular to the chain direction $g'(\lambda) \equiv g_{\perp}(\lambda)/\epsilon$. As a result, the conductance becomes isotropic by construction and 3D scaling theory can be used to calculate the conductance of a macroscopic sample. The electronic correlation length is given by $\xi = \lambda[(\zeta/a)\exp(-\lambda/\zeta) - g_c]^{-\nu}$, which immediately shows that a metallic state only exists beyond a critical interwire coupling

$$\epsilon_c = a/(\zeta \ln[\zeta/(ag_c)]). \quad (9)$$

Calculation of σ is now straightforward. Using Eq. (4), the conductivity in the metallic regime is found to be

$$\sigma_M = \frac{e^2}{\hbar} \frac{Aa}{4b^2} g_c \left(\frac{\zeta}{a} e^{-\lambda/\zeta} - g_c \right)^{\nu}. \quad (10)$$

In the localized regime, $g(\lambda) < g_c$, the conductivity of a cube of dimension $L \gg \xi$ is obtained from Eq. (5) as

$$\sigma_1(L) = \frac{e^2}{\hbar} \frac{a\lambda}{4Lb^2} g_c \exp\left(-\frac{BL}{\lambda} \left| \frac{\zeta}{a} e^{-\lambda/\zeta} - g_c \right|^{\nu}\right). \quad (11)$$

Let us now apply these results to model transport in conducting polymers. Four PPy samples were prepared at temperatures between -40°C and 25°C [3]. The dc conductivity of this system is shown in Fig. 1. PPy samples A and B are in the metallic regime, sample C lies at the boundary of the metal-insulator transition, and sample D is clearly in the insulating regime. Also shown are data for PAc [5], H_2SO_4 doped PPV [6], and SWNT mats [8] and ropes [7]. The various systems reveal similar behavior: $d\sigma/dT > 0$ over a broad T range, even in the metallic regime. As the above model is limited to $T = 0$, first the influence of temperature is discussed.

A first effect of temperature is dephasing. A metal-insulator transition is a $T = 0$ quantum phase transition [11]. Dephasing cuts off scaling: the system becomes classical above the dephasing length L_{Φ} . Dephasing results from inelastic scattering events with rate $\propto T^p$ where $p > 1$ [11], or from spontaneous symmetry breaking of the quantum coherent state with rate $\sim k_B T/\hbar$. The latter reflects the transition is gapless: modes with energy $< k_B T$ become occupied by many quanta so the system stays quantum coherent only for times $< \hbar/k_B T$ [11]. For weak coupling, transport remains strongly 1D, and inelastic scattering occurs via Umklapp processes. For electron-electron interactions this is prohibited by conservation laws, while for electron-phonon scattering the probability is exponentially small due to negligible phonon occupation

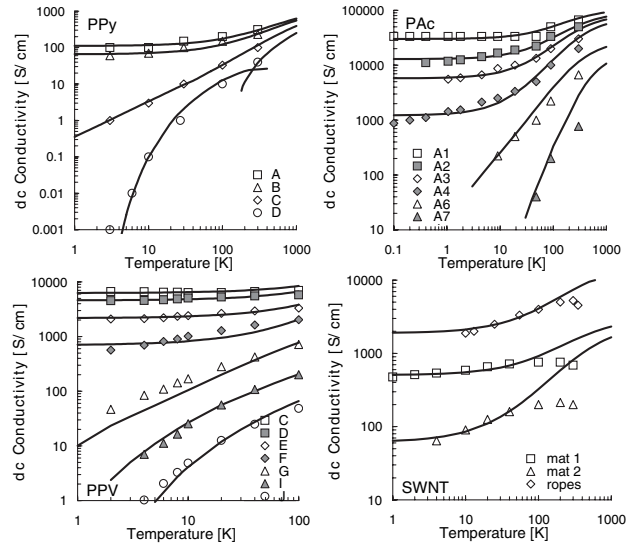


FIG. 1. Conductivity of PPy [3], PAc [5], PPV [6], and SWNT [7,8] fitted with theoretical curves (solid lines) for coherent transport in coupled disordered wires.

at energy $\sim 2E_F$. Thus, one dimensionality should lead to long L_{Φ} . Here, it is assumed that $L_{\Phi} > \xi$ (low T). In the metallic phase, scaling remains Ohmic and Eq. (10) will not be affected. In the insulating phase, the conductivity is obtained by substituting the appropriate value of $L_{\Phi}(T)$ in Eq. (11). A full calculation of $L_{\Phi}(T)$ for 1D wires has not yet appeared [12] and we will restrict ourselves to a heuristic argument for $L_{\Phi}(T)$: temperature introduces a dephasing rate $\sim k_B T/\hbar$: a fraction T/T_0 of the carriers is dephased, with $k_B T_0$ an energy scale of the order of the Fermi level. This suggests $L_{\Phi} = aT_0/T$.

A second effect of temperature is the increase of coherent coupling. Moško *et al.* [12] demonstrated an increase of coherent conductance with temperature in disordered wires, which they attributed to the availability of resonant tunneling channels in a window of several $k_B T$ around the Fermi level. Also here, thermal broadening of the electronic Fermi-Dirac distribution can open additional resonant channels between states on adjacent wires. At low T the probability for this mechanism is $\sim k_B T/\Delta$ which can be seen as an additional coupling mechanism. Hence, we assume a temperature dependent coupling amplitude $\epsilon(T) = \epsilon_0 + k_B T/\Delta = \epsilon_0 + k_B T N \zeta$.

Using this theory, $\sigma(T)$ data shown in Fig. 1 are well reproduced ($\nu = 1$, $A = 1$, $B = 0.2$). Note that $d\sigma/dT < 0$ behavior as observed for some systems is not captured by the present theory. PPy data reported by Yoon *et al.* [4] and Ishiguro *et al.* [5] were fitted successfully with similar values (not shown). For *all* samples the same microscopic parameters are used. PPy: density of states $N = 0.6 \text{ eV}^{-1} a^{-1}$ [4], intrachain lattice constant $a = 7.1 \text{ \AA}$, and interchain separation $b = 3.4 \text{ \AA}$ [13]. PAc: $N = 1 \text{ eV}^{-1} a^{-1}$, $a = 3 \text{ \AA}$, $b = 4 \text{ \AA}$. PPV: $N = 0.5 \text{ eV}^{-1} a^{-1}$, $a = 8 \text{ \AA}$, $b = 3.6 \text{ \AA}$. SWNT: $N = 2 \text{ eV}^{-1} a^{-1}$, $a = 16.5 \text{ \AA}$, $b = 3.4 \text{ \AA}$. For PAc a factor 50 increase in con-

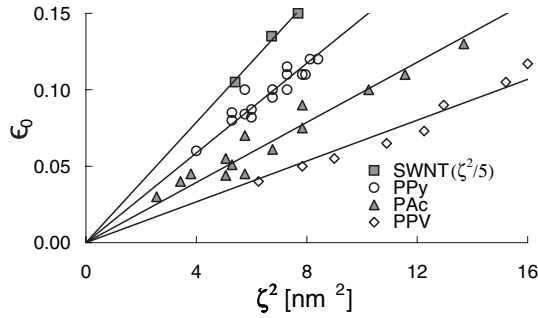


FIG. 2. Dependence of interchain coupling ϵ_0 on squared intrachain localization ζ^2 in SWNT, PPy, PAC, and PPV.

ductivity along the stretch direction was assumed. For PPV a factor 20 increase along stretching direction gradually decreased upon aging reflecting the material degradation [6]. Thus, for all materials analyzed here, the individual samples are fully characterized by an intrachain localization length ζ and $T = 0$ interchain coupling ϵ_0 , see Fig. 2; for clarity ζ^2 of SWNT has been scaled by a factor 0.2.

We can push our analysis further by realizing that ϵ_0 is governed by the interchain transfer I_{\perp} and the energy mismatch between adjacent states $\sim \Delta/2$. For $I_{\perp} < \Delta/2$, the mixing amplitude is $\epsilon_0 = 4I_{\perp}^2/\Delta^2 = 4I_{\perp}^2 N^2 \zeta^2$. Indeed, Fig. 2 shows a clear linear dependence of ϵ_0 on ζ^2 . This demonstrates that the variation of ϵ_0 can be fully accounted for by disorder: in these systems the disorder impacts both intrachain localization and interchain coupling. From the fits $I_{\perp} = 0.09, 0.07, 0.03$, and 0.05 eV is obtained for SWNT, PPy, PAC, and PPV, respectively, in excellent agreement with calculations [14,15].

The question posed in the introduction can now be answered. From Eq. (9) and the above result, a criterion, given by Eq. (1), for the formation of a macroscopic metallic state in disordered coupled wires is obtained. To very good accuracy, it corresponds to a power law dependence $I_{\perp} \propto \Delta^{1.6}$. It is tempting to compare this to the numerical findings $W \propto I_{\perp}^{0.61}$ [2] coinciding with the present result when $\Delta \propto W$ as expected for relatively strong disorder $W > I_{\parallel}$. From Eq. (1) it is concluded that full delocalization requires at least one resonant interchain transition within the intrachain localization length. Application to PPy illustrates the power of this result: the number of resonant interchain transitions per intrachain state drops from 1.08 for sample A to 1.02, 0.87, and 0.63 for samples B, C, and D, respectively, explaining the metal-insulator transition.

One aspect that has not yet been considered is the heterogeneous structure of conducting polymers. Structural analyses show the coexistence of “crystalline” islands and amorphous areas [16]. This may result in spatially separated localized and delocalized states [17]. For a metallic state, a macroscopic network of crystalline regions is required. Indeed, the best conducting polymers have high crystallinity $\sim 50\%$ [16], well above the percolation threshold. Then, the dc transport is dominated by the conductive

properties of the crystalline regions (that shortcut amorphous areas), which we recently argued is limited by interchain transitions [10]. The theory presented here describes the coherent transport between coupled 1D wires. When this is the limiting transport mechanism, inhomogeneity merely adds a geometric correction factor to Eqs. (10) and (11), which is close to unity for high-quality polymers well above the percolation threshold. For lower crystallinity, amorphous phases interrupt the network and conduction will be dominated by hopping transport between crystalline islands [10,17]. Thus, the metal-insulator transition results from two complementary processes: at the macroscopic level a connected network of well-ordered regions should be present while at the microscopic level interwire coupling should overcome the intrinsic 1D localization within these regions.

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