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LETTER TO THE EDITOR

The Anderson transition in a model of coupled random polymer chains

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Abstract. We obtain by transfer matrix scaling methods the Anderson metal–insulator phase diagram for a random electronic tight binding Hamiltonian, modelling a 'spaghetti' of random polymer chains having randomly placed cross-links J with concentration c. If J is small and c is large the results depend on the product $J \cdot c$ as predicted by a mean-field approach. For large J and small c this dependence breaks down as a result of the large off-diagonal disorder introduced by the random cross-linkings. The localization length critical exponent in this highly anisotropic model takes the universal three-dimensional value $\nu = 1.3 \pm 0.2$.

In spite of several decades of intensive research, the field of strong localization (i.e. of disorder-induced transition from propagating to trapped waves) is still open to question. The reason is the lack of conclusive experiments and the absence of rigorous theoretical results even in the most simplistic models. It is still of interest to look for new materials which exhibit controllable disorder-induced (also referred to as Anderson) metal–insulator transitions (MIT) and for models allowing rigorous results. Recently, attention has been focused on the highly conducting conjugated polymers which seem to undergo a MIT driven by disorder. Relevant experimental results on these materials are accumulating [1, 2, 3] and a theoretical treatment [4] was recently developed via a rather realistic model, which extends and enriches the widely used basic Anderson model [5].

In conducting conjugated polymers, disordered chains couple into fibrils which in turn form a cross-linked network. The most prominent characteristic concerning their electronic properties is the high conductivity obtained upon doping [1, 2, 3]. On the other hand, the experimental observations in highly doped $(CH)_x$ polymer fibrils [2] reveal a negative magnetoresistance, which agrees with the fact that for an individual fibril the presence of structural defects and dopant ions will eventually result in localization of its electronic states. It is only when electron transfer is permitted among the fibrils that extended states and conducting properties may appear, which is experimentally seen as a change of sign in the magnetoresistance. Therefore, one expects to obtain an Anderson MIT by varying the degree of disorder and/or the concentration of the cross-links and/or the hopping probability between the random chains. In fact, as recent experiments [1, 2, 3] suggest, the highly conducting conjugated polymers are very close to the MIT boundary.

We propose a very simplified model for the cross-linked polymer network which, nevertheless, incorporates the interchain hopping and has theoretical interest of its own because it exhibits novel and unexpected behaviour for certain regions of values of the parameters. The random interchain linking restores the three-dimensional (3D) nature of the system but at the expense of an additional strong off-diagonal disorder. It is exactly

the conflicting aspects of the 3D connectivity and the off-diagonal disorder which make the model very interesting and limit the applicability range of the MFT [4]. We treat the conjugated polymers as quasi-one-dimensional systems consisting of coupled linear chains [9], by introducing an anisotropic tight-binding simple cubic lattice with one orbital per site indexed by l, n, m. The diagonal matrix elements $\varepsilon_{l,n,m}$ are independent random variables having a rectangular probability distribution of total width W and the nearest-neighbour intrachain (longitudinal) hopping matrix element V is taken as the unit of energy. The nearest-neighbour interchain (perpendicular) hopping matrix element is equal to J with probability c and zero with probability $1 - c$. Thus, the concentration of junctions per unit length is $p = 4c/a$, where a is the lattice spacing taken as the length unit. For $c = 0$ the random chains uncouple and the one-dimensional ($d = 1$) limit is recovered where no extended states are expected. The $c = 1$ limit, instead, corresponds to the usual $d = 3$ isotropic for $J = 1$ or anisotropic for $J \neq 1$ disordered solid, for which an Anderson transition exists at a finite value of the disorder [8]. Therefore, our model has four parameters: the usual on-site (diagonal) disorder whose strength is denoted by W, the energy E, the concentration c of the cross-links between the chains and the interchain transfer matrix element J. Our aim is to determine the position of the Anderson MIT and also to obtain the corresponding critical behaviour in order to treat with confidence regions in the parameter space inaccessible to the MFT approach of [4].

The difference equations obeyed by the amplitudes $\alpha_{l,n,m}$, for a bar of length L and square cross-section $M \times M$, take the form

$$(E - \varepsilon_{l,n,m})\alpha_{l,n,m} = V(\alpha_{l-1,n,m} + \alpha_{l+1,n,m}) + J'^{l,n-1,m}_{l,n,m}\alpha_{l,n-1,m} + J'^{l,n+1,m}_{l,n,m}\alpha_{l,n+1,m}$$

$$+ J'^{l,n,m-1}_{l,n,m}\alpha_{l,n,m-1} + J'^{l,n,m+1}_{l,n,m}\alpha_{l,n,m+1} \qquad (1)$$

with $P(\varepsilon) = 1/W$ for $|\varepsilon| < W/2$ and $P(J') = c\delta(J' - J) + (1 - c)\delta(J')$, $l = 1, 2, ..., L$, $n, m = 1, 2, ..., M$. It can be shown analytically and verified numerically [6, 7, 8] that the quantity $\langle \ln|\alpha_{1,n,m}/\alpha_{L,n,m}|\rangle$ for $L \to \infty$ equals either $\gamma_i L$ or $-\gamma_i L$, with $i = 1, 2, ..., M^2$. These define the Lyapunov exponents $0 \leqslant \gamma_1 \leqslant \gamma_2 ... \leqslant \gamma_{M^2}$, which are functions of E, W, c, J and M. If the smallest exponent $\gamma_1 > 0$, the corresponding eigenstate is localized, for the given bar, with a localization length λ_M equal to the inverse, γ_1^{-1}. The Lyapunov exponents can be obtained numerically [6, 7, 8] from the eigenvalues of the $L \to \infty$ product of the consecutive transfer matrices connecting the $\alpha_{l-1,n,m}, \alpha_{l,n,m}, n, m = 1, ... M$ amplitudes with the $\alpha_{l,n,m}, \alpha_{l+1,n,m}(n, m = 1, ...M)$, for each l. In the numerical work L was sufficiently large (at least 5000) and λ_M was computed as an average over 20 different samples. The numerical error is given by the standard deviation of the corresponding mean value which was required to be less than 1% in most cases. More details on how the numerical work is done and the scaling curves computed will appear in a forthcoming publication [10].

According to the checked one-parameter scaling hypothesis, the quantity λ_M/M for sufficiently large M is a function of M/λ only, where the M-independent characteristic length λ equals the localization length $\lambda \equiv \lim \lambda_M$ as $M \to \infty$, if the states are localized and characterizes the extent of the largest amplitude fluctuation if the states are extended. In the case of large anisotropy we found that quite large values of M were needed in order to obtain reliable results, so it was essential to extend our numerical calculations up to $M = 17$. In the localized regime $W > W_c(E, J, c)$ and for sufficiently large M we find that λ_M/M is a decreasing function of M, while in the extended regime $W < W_c(E, J, c)$ it rises with M. At the critical point $W = W_c$, the ratio is a constant $(\lambda_M/M)_c$. Following the numerical procedure outlined above, we determined the critical value of $W_c = W_c(E, c, J)$, the $(\lambda_M/M)_c$ and the critical exponent ν defined from the relation $\lambda \sim |W - W_c|^{-\nu}$ as
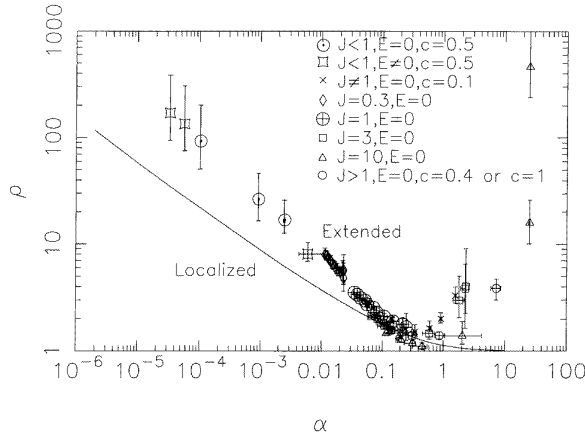
Figure 1. Critical points of the metal–insulator transition according to the present calculations are compared with the results of [4] (solid line). See text for the definition of the various symbols.

$W \to W_c$, via the reciprocal of the slope of the linear relationship between the $\ln\left[\frac{\mathrm{d}(\lambda_M/M)}{\mathrm{d}W}\right]$ and $\ln M$ at $W = W_c$ [10].

We attempt to compare our results for the $W_c = W_c(E, c, J)$ with the ρ versus α phase diagram shown in figure 2 of [4], where $\rho = 4pR_{loc}$ and $\alpha \equiv (\pi\tilde{\nu}J)^2$ with R_{loc} the localization length of the fibril, $\tilde{\nu}$ the density of states per unit of fibril length and $p = 4c$. It should be noted that this should be, at most, a semi-quantitative comparison since in our model the fibrils are replaced by single chains. As a result, the density of states $\tilde{\nu}$ must be replaced by its 1D value $\tilde{\nu}_1$, which may differ substantially from $\tilde{\nu}$, especially for weak disorder and near the band edge. Moreover, the fibril localization length $R_{loc} = 2\pi\hbar\tilde{\nu}D$, where D is the diffusion coefficient of the fibril. If the number of chains in the fibril approaches one and the disorder is weak, R_{loc} becomes less than the one-dimensional localization length λ by a factor of 3.75 at the band centre and 6 at the band edge. In order to make a more meaningful comparison with the MFT we have taken into account this factor, so that $\rho \equiv 4c\lambda$ and $\alpha \equiv (\pi\tilde{\nu}_1 J)^2$ without any adjustment, are used in the comparison.

In figure 1 our results for the ρ versus α phase diagram are shown. If $J \leqslant V$ the data are in qualitative agreement with those of [4], in the sense that the four parameters W, c, E and J have collapsed into two, namely ρ and α, and the obtained critical line $\rho = f(\alpha)$ follows reasonably well (given the differences of the two models) the trends of the analytical curve of [4]. Furthermore, for smaller J this agreement extends beyond the regime $(4c)^2 \ll 1$, corresponding to the inequality (1) of [4], in agreement with the conjecture of Prigodin and Efetov that it should be qualitatively correct for the whole region of parameters. However, for large J and small c (in fact, when $(1-c)J^2 \gg V^2$) strong qualitative departures from the MFT appear. In this large-J regime, which starts from lower values of J if c becomes smaller, by increasing J the states become more easily localized instead of more extended. This is shown in figure 1 where the critical points turn upwards for large α and become more scattered. It must be also pointed out that our results seem to be in a reasonable agreement, for the whole region of parameters, with a recent non-linear σ-model approach for the same model [11].
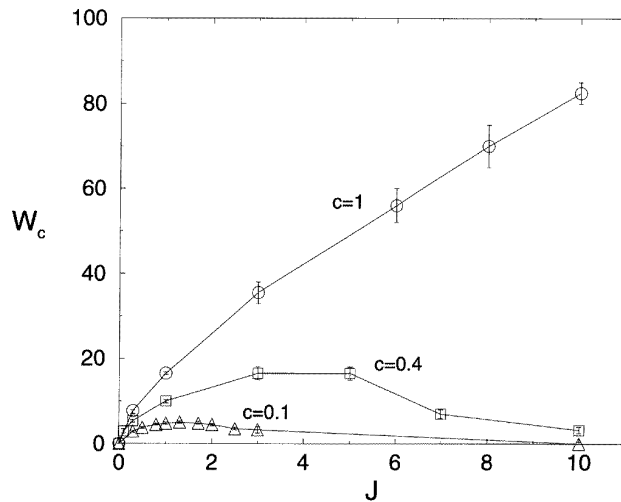
Figure 2. The critical value of the disorder W_c at the band centre $E = 0$ as a function of J is shown for three different concentrations c.

In figure 2 the critical value of the disorder W_c at $E = 0$ is plotted against J for different values of c. It is shown that for very large values of c approaching one W_c is monotonically increasing with J (if $J \leqslant 10$). If c is smaller then W_c reaches a maximum as J increases from zero to $J_m(c)$ and beyond this value it decreases monotonically with J. The reason for this rather unexpected behaviour, already indicated for large α in figure 1, is due to the dual role played by J. This provides alternative paths for propagation (transforming the one-dimensional system to a quasi-three-dimensional system by increasing the critical disorder required for localization) and on the other hand, for $c \neq 1$, it creates an additional scattering mechanism in the form of off-diagonal disorder which facilitates localization. For large values of J and $1 - c$, the second role dominates leading to a decreasing W_c with J. We have also calculated [10] the critical exponent ν and the critical value of $(\lambda_M/M)_c$, for various sets of parameters. We find that ν takes the universal value 1.3 ± 0.2 independently of c and J/V while for the isotropic case transfer matrix results give $\nu = 1.4 \pm 0.3$ even in the presence of a random magnetic field in three dimensions [17]. There is no experimental estimate of ν for conjugated polymers, to the best of our knowledge.

In [4] it was speculated that the critical line for a given energy E has the form

$$J \cdot c = f(W_c) \tag{2}$$

with the product $J \cdot c$ playing the role of an effective bandwidth in the transverse direction. This is close to our results, for not so large $(1 - c)J^2$. For $J \leqslant V$ we found the simple expression

$$W_c \approx 16V^{1-\kappa} J^\kappa c^\mu \tag{3}$$

with both κ and μ around 0.5 (e.g. for $J = V$ the exponent is $\mu = 0.53 \pm 0.03$ while for $J = 0.3V$ it is $\mu = 0.43 \pm 0.03$). It is worthwhile to mention that previous self-consistent [12] and perturbative calculations [16] performed in the context of an anisotropic lattice Hamiltonian [12–16] gave $\mu = 1/2$. However, for $J \gg V$ and small c, (2) is clearly violated as shown in figure 3. Indeed the $J \cdot c$ dependence of the critical value, W_c, in this regime is quite complicated. On the basis of the physical arguments for the dual role of J
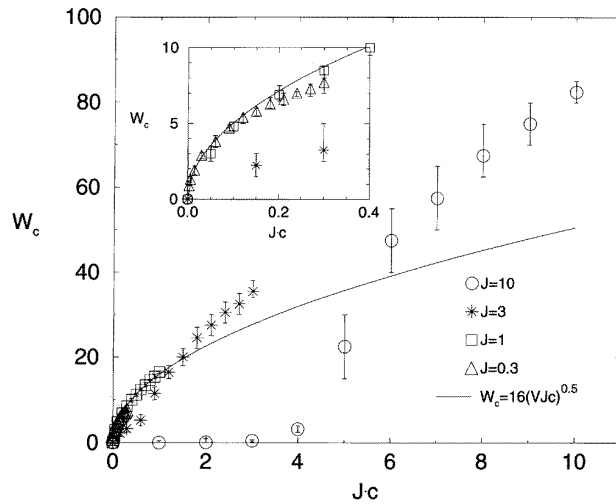
Figure 3. The $J \cdot c$ dependence of the critical disorder W_c at the band centre $E = 0$ for various values of J (inset: detail of the region $J \cdot c \leqslant 0.4$).

we expect that the W in (2) should be replaced by an effective total disorder $\tilde{W}$ such that

$$\tilde{W}^2 = g(W^2; J^2(1 - c)) \tag{4}$$

where $\tilde{W}$ is an increasing function of both the pure diagonal disorder W and the induced effective diagonal disorder $J^2(1 - c)$. If J is not so large one might assume an additive relationship, i.e. $\tilde{W}^2 = W^2 + A(1 - c)J^2$, where A does not depend on J.

   In summary, we studied via a reliable numerical technique the electronic propagation in a model incorporating the essential features of disordered cross-linked conjugated polymers and exhibiting very interesting behaviour of its own. In this model, the polymer chains are represented by linear tight-binding disordered chains, coupled by randomly placed interchain matrix elements with concentration c, having magnitude J. These matrix elements establish the 3D character in the model, at the expense of introducing strong off-diagonal disorder. For small J and large c, our results seems to confirm the validity of a recent MFT [4], which essentially replaces the off-diagonal random matrix element by its average $J \cdot c$. For large J and small c the MFT breaks down and the critical point is not only a function of the product $J \cdot c$ as proposed in [4]. However, the MFT quasi-universality, in the sense that the four parameters J, c, E and W collapse into two, may also be valid in the large-J, small-c regime where large fluctuations in the numerical results are shown (figure 1). However, there is a better agreement, even in the $\alpha \gg 1$ regime, with recent analytical results based on a non-linear σ-model approach [11]. Moreover, the obtained localization length critical exponent $\nu = 1.3 \pm 0.2$ is consistent with the value obtained in the usual 3D isotropic Anderson model within numerical errors. Many interesting questions remain open in this area, such as the extension of our model to describe the fibrils more realistically (not as single chains) and the inclusion of a magnetic field.

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