

Metal-insulator transition in PF₆ doped polypyrrole: Failure of disorder-only models

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The free-carrier scattering time and plasma frequency in PF₆ doped polypyrrole near the metal-insulator transition (MIT) is obtained by dielectric spectroscopy (8–700 GHz) down to 2 K. The specific T -dependence allows us to quantify the distance to the MIT for both metallic and insulating samples. The evolution of the free-carrier parameters when going deeper into the metallic regime conflicts with both the homogeneous and heterogeneous disorder models. We suggest this failure to stem from the interplay between electronic correlations and interchain charge transfer, which is not explicitly considered in these theories.

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In general the occurrence of a metal-insulator transition (MIT) depends on several parameters.¹ In the absence of electron-electron interactions a random potential W localizes charge carriers due to the interference of multiply-scattered electronic waves.² For this process the scaling theory of Anderson localization provides a convenient framework.³ Often electron-electron interactions suppress the conductivity and eventually lead to the Mott-Hubbard MIT.⁴ As reduced dimensionality enhances the effects of disorder and interactions,³ the geometry of the electronic system plays a profound role as well. For instance, in a strictly one-dimensional system for any amount of disorder all states are localized due to repeated backscattering.⁵ In doped conjugated polymers, it is widely recognized that structural disorder drives the MIT,^{6–9} while recent observations of density wave dynamics point to the importance of electronic correlations.¹⁰ On a microscopic scale charge transport is inevitably anisotropic: the charge transfer perpendicular to the chain is weak compared to that along the chain, which enhances the effects of disorder and electronic correlation. Nonetheless, a positive temperature coefficient of the resistivity^{6,11} and a negative dielectric constant in the microwave and far-infrared regime^{7,12} indicate the presence of a truly metallic state. In a previous study we pointed out a correlation between the plasma frequency ω_p and scattering time τ which together characterize the free-carrier dynamics.¹² To explain the required finite density of delocalized states at the Fermi-level interchain charge transfer had to be sufficiently strong to overcome the disorder- and interactions-induced localization.¹²

In the present work we extend the dielectric measurements as a function of frequency $\omega = 2\pi f$ on PF₆ doped polypyrrole (PPy) around the MIT from 300 K to 2 K. The specific T - and ω -dependent response enables the characterization of the position with respect to the MIT for both insulating and metallic samples. We evaluate the dependence of ω_p and τ as a function of this distance, especially the strong decrease of τ when going deeper into the metallic phase is in conflict with the usually applied disorder-only models for the MIT. This discrepancy provides a strong clue for the role of interchain coupling and electronic correlation.

Free-standing films of PPy-PF₆ are prepared by electrochemical polymerization as described in detail elsewhere.^{6,8} Films have been polymerized at different temperatures ($-40^\circ\text{C} < T_{\text{pol}} < 20^\circ\text{C}$). One sample (D) has been slightly dedoped after the synthesis. The dc conductivity (σ_{dc}) of several samples is shown in Fig. 1. The plot of the reduced activation energy $W = d \ln(\sigma_{\text{dc}}) / d \ln(T)$ versus T , Fig. 1(b), demonstrates that samples in the metallic ($M2, M$), critical (C), and insulating (I) regime of the MIT are obtained. Sample $M2$ ($T_{\text{pol}} = -40^\circ\text{C}$) exhibits a conductivity minimum around 13 K, below which $\partial\sigma_{\text{dc}}/\partial T < 0$ indicating truly metallic behavior. However, for both M and $M2$, $\partial\sigma_{\text{dc}}/\partial T \geq 0$ at higher T which shows that PPy-PF₆ is at best a “bad” metal. For increasing T_{pol} , the conductive properties deteriorate and the system goes through the MIT. This can be attributed to an increase of the structural disorder.⁶

The electrodynamic properties have been studied by means of transmission experiments¹³ in the frequency range 8–700 GHz ($0.27\text{--}23\text{ cm}^{-1}$, $0.033\text{--}2.9\text{ meV}$), which overlaps with both the microwave and far-infrared regime. Both amplitude and phase are obtained by means of an ABmm vector network-analyzer. The data are fitted to first-principle transmission formulas to derive the complex conductivity $\sigma^*(\omega) = \sigma(\omega) + i\omega\epsilon_0\epsilon(\omega)$, without the use of Kramers-Kronig manipulation.¹³ Uncertainty in σ and ϵ is less than 5% in the range 100–600 GHz at all T .

The T -dependent $\epsilon(\omega)$ of C and M are shown in Fig. 2.

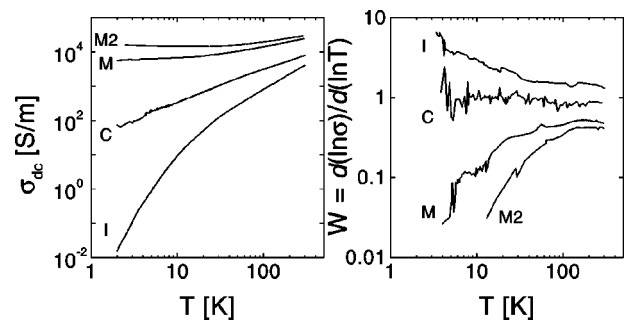


FIG. 1. T dependence of σ_{dc} (left) and the reduced activation energy $W = d \ln(\sigma_{\text{dc}}) / d \ln(T)$ (right).

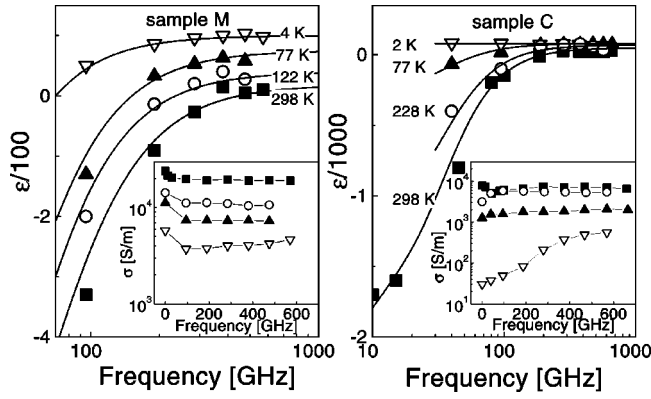


FIG. 2. T dependence of $\varepsilon(\omega)$ of M and C . Solid lines are fits to the Drude model. The insets show $\sigma(\omega)$ of M and C at the same T . Error bars are less than the symbol size.

For C , $\varepsilon < 0$ only at high T , while for M a negative contribution to $\varepsilon(\omega)$ persists down to low T . The negative ε agrees with the findings of Kohlman and co-workers,⁷ and establishes the presence of free carriers in PPy-PF₆. Solid lines are fits to the Drude model:

$$\varepsilon(\omega) = \varepsilon_b - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}, \quad (1)$$

with τ the free-carrier scattering time, ε_b the background dielectric constant due to polarization of the lattice and localized carriers, and ω_p the plasma frequency:

$$\omega_p = \sqrt{\frac{n_f e^2}{\varepsilon_0 m^*}}, \quad (2)$$

with n_f the free-carrier density, e electronic charge, m^* the effective mass, and ε_0 the vacuum permittivity. The insets of Fig. 2 show $\sigma(\omega)$ for C and M at the same T 's. Note that for M , $\partial\sigma/\partial\omega < 0$ at low ω at all T as expected for free carriers, while for C only at room temperature $\partial\sigma/\partial\omega < 0$ is observed.

By fitting to Eq. (1), the $\varepsilon(\omega, T)$ data lead to $\omega_p(T)$ as shown in Fig. 3(a). The T -dependent data do not extend to low enough ω to derive τ from $\varepsilon(\omega)$. However, according to Drude the metallic contribution to σ_{dc} equals $\omega_p^2 \tau \varepsilon_0$, which is estimated by $\sigma_{dc} - \sigma(95 \text{ GHz})$ for M , see inset of Fig.

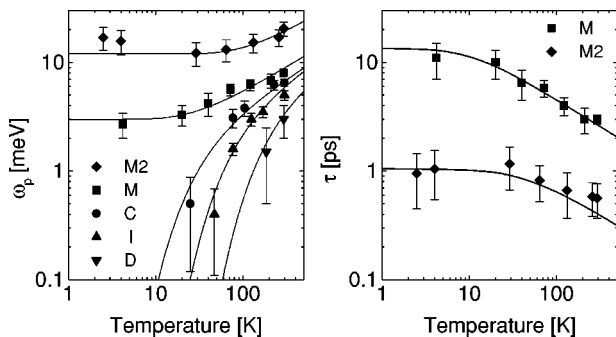


FIG. 3. ω_p (left) and τ (right) as a function of T . Solid lines are explained in the text.

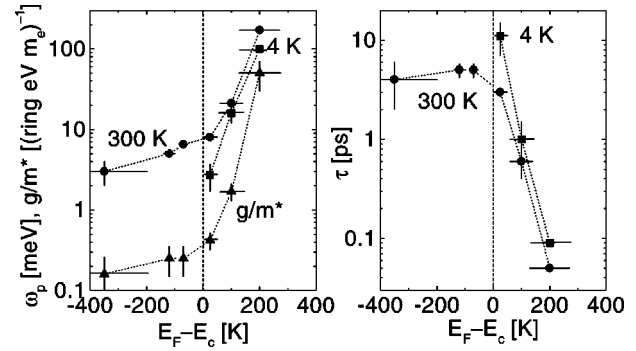


FIG. 4. Dependence of ω_p , and τ on $(E_F - E_c)$ at $T=300 \text{ K}$ (dots) and $T=4 \text{ K}$ (squares). Also included are PPy-PF₆ data taken from Ref. 7. The dependence for g/m^* (triangles) is shown in the left panel. The metallic and insulating regimes are characterized by $E_F - E_c > 0$ and < 0 , respectively. Dotted lines are guides to the eye. Error bars are indicated, or less than the symbol size.

1(a), and $\sigma_{dc} - \sigma(500 \text{ GHz})$ for $M2$.¹² For metallic M and $M2$, $\tau(T)$ could thus be obtained, see Fig. 3(b).

First we consider the behavior of $\omega_p(T)$ near the MIT. For $M2$ and M , ω_p decreases when cooling but remains finite at low T : for these metallic samples free carriers are present at $T=0$. For C , I , and D , ω_p strongly drops when lowering T which shows that $n_f \rightarrow 0$ as $T \rightarrow 0$. In comparison with conventional metals where $\omega_p \sim 1-10 \text{ eV}$, the ω_p 's in PPy-PF₆ are very low. For these systems near the MIT only a fraction of the carriers occupies extended states (0.1% if m^* equals the free electron mass m_e ; a larger m^* would imply a larger n_f) with the majority of the carriers residing in localized states.^{7,12} The observed increase of ω_p with T of both the metallic and insulating samples shows that barely localized carriers can be thermally activated to higher-lying extended states. Irrespective of the localization mechanism, there will be a critical energy (E_c) separating the lower-lying localized states and the higher extended states.^{12,14} Then, for given Fermi-level E_F , the density of occupied extended states follows from

$$n_f(T) = \int_{E_c}^{\infty} f_{FD}(T) g(E) dE, \quad (3)$$

where f_{FD} denotes the Fermi-Dirac distribution function, $g(E)$ is the density of states, and E_F is defined as zero. Using Eqs. (2) and (3) and assuming that m^* is independent of T and that g is independent of E , the $\omega_p(T)$ data sets for each sample can be excellently reproduced [solid lines in Fig. 3(a)] with only two free parameters: $E_F - E_c$ and g/m^* . The T -dependence of ω_p is fixed by $E_F - E_c$; the absolute value is fixed by both. For samples $M2$, M , C , I , and D $E_F - E_c$ is found to be: $100 \pm 50 \text{ K}$, $25 \pm 10 \text{ K}$, $-70 \pm 15 \text{ K}$, $-120 \pm 20 \text{ K}$, and $-350 \pm 150 \text{ K}$, respectively; values for g/m^* are presented in Fig. 4. Analysis of the PPy-PF₆ data given in Ref. 7 gives $E_F - E_c = 200 \pm 100 \text{ K}$. As expected, for metallic samples $E_F > E_c$, while for C , I , and D , $E_F < E_c$. While previous studies resorted to the so-called resistivity ratio¹⁵ the above results provide an experimental characterization of the conductive state

with respect to the MIT in terms of a physical quantity. To our knowledge, for conducting polymers a comparable quantitative analysis has not been reported, and, as demonstrated below, provides a new perspective on the mechanisms behind the MIT.

Let us now turn to the derived τ 's, see Fig. 3(b). In view of commonly reported $\tau \sim 10^{-14}$ s values in normal metals, the scattering times in the disordered PPy-PF₆ are extremely long. If all carriers were delocalized in a three-dimensional band,⁷ and hence $v \approx \sqrt{2E_F/m^*} \approx 5 \times 10^5$ m/s, these long τ 's lead to anomalously long mean free paths $l \approx 0.2$ μ m and 2 μ m for *M2* and *M*, respectively. However, only above E_c carriers are mobile, hence the free-carrier velocity does not depend on the total carrier density but only on the density of free carriers above E_c .¹⁶ In conformance with the ω_p analysis, the proper T -dependent carrier velocity is $v = n_f^{-1} \int_{E_c}^{\infty} f_{FD} g \sqrt{(E - E_c)/m^*} dE$. Up to a proportionality factor, the T -dependence of v is fixed by the value of $E_F - E_c$, which follows from the ω_p vs T -data; the value of $E_F - E_c$ enters via f_{FD} . If l is constant, the T dependence of the scattering times $\tau = l/v(T)$ can be calculated [solid lines in Fig. 3(b)]. These lines reproduce the data well, although for *M2* the agreement is ambiguous due to the error bars. The T -independence of l suggests that static-disorder scattering is dominant. If $m^* = m_e$, $l = 20$ nm, and $l = 200$ nm for *M2* and *M*, respectively (larger m^* would give shorter l). This apparent decrease of l in less disordered, better conducting samples already point to a shortcoming of disorder-only models.

Figure 4 shows ω_p and τ versus $E_F - E_c$ at 300 K and 4 K together with the ratio g/m^* versus $E_F - E_c$, and is the main result of our study. The free-carrier parameters clearly correlate with the distance to the MIT: a strong dependence in the metallic regime, and a weaker dependence in the insulating regime. First, let us consider the growth of ω_p with $E_F - E_c$. In the insulating regime the free-carrier density depends on the thermal activation of barely localized carriers: the less negative $E_F - E_c$ is the easier it becomes to occupy extended states and the higher ω_p will be. For $T \rightarrow 0$, only in the metallic regime a free-carrier density survives and, according to Eqs. (2) and (3), $\omega_p = \sqrt{(E_F - E_c)g e^2 / \epsilon_0 m^*}$. In the metallic regime the increase of ω_p is clearly stronger than $(E_F - E_c)^{1/2}$. This implies that g/m^* , which stays nearly constant in the insulating regime, rises over a factor of 100 when traversing the MIT, see Fig. 4, i.e., g increases and/or m^* decreases with increasing metallicity. This thresholdlike behavior suggests the properties of extended electronic states to change abruptly at the MIT. Given that $g \sim 1-10$ states/(eV ring),^{7,15,17} we estimate m^* to be in the $1-10 \times m_e$ range.

The dependence of τ on $E_F - E_c$ seems peculiar: when coming from the insulating regime and crossing the MIT τ drops sharply. This behavior persists in both the degenerate, $(E_F - E_c) > k_B T$, and nondegenerate, $(E_F - E_c) < k_B T$, regimes and agrees with a recently pointed out empirical correlation $\tau \propto \omega_p^{-x}$ ($x \sim 1.3$) over two orders of magnitude

ω_p -range.¹² Below we will argue that these results contradict the disorder-only models⁶⁻⁹ and propose a possible solution to this discrepancy.

According to the scaling theory of Anderson localization,³ $E_F - E_c$ increases when the amplitude of the disorder potential decreases, and $l \propto (E_F - E_c)^p$ with $p > 0.5$,¹⁶ becomes larger. Hence, Anderson theory gives $\tau = l/v \propto (E_F - E_c)^{p-1/2}$ which is a monotonically increasing function for $E_F > E_c$ and therefore conflicts [Fig. 4(b)]. Furthermore, strong changes of g and m^* are not expected if only the strength of the disorder potential varies. Thus, the homogeneous disorder model is in conflict with our experimental observations. It has been proposed that the MIT in conducting polymers is better viewed in terms of percolation of metallic islands.^{7,9} Then $E_F - E_c$ characterizes the barrier heights between the metallic domains and depends on the concentration of these domains. In a percolating metallic network τ corresponds to either the intrinsic free-carrier scattering time within the metallic islands, and is then independent of $E_F - E_c$, or reflects scattering due to finite-size effects. In this latter case, an increase of $E_F - E_c$ should lead to an increase of τ as well, due to the improved connectivity of the network. Furthermore, the free-carrier parameters g and m^* are in this case properties of the metallic islands themselves, and can not depend on the distance to the MIT (concentration of such islands). Therefore, also the heterogeneous model can not account for the experimental results shown in Fig. 4. Clearly, we must conclude that the free-carrier dynamics in the metallic regime can not be understood in terms of the disorder-only schemes.⁶⁻⁹

In both the homogeneous and heterogeneous disorder models the intrinsic anisotropy of electronic transport is ignored. Nonetheless, even in the absence of disorder, to obtain a *macroscopically* conducting state interchain charge-transfer t_c is a prerequisite: in the limit of vanishing t_c carriers are bound to individual polymer chains giving rise to an insulating state. A small t_c will impede the formation of a metallic state as will be visible in the low-frequency conductive properties.¹⁸ To explain the effect of t_c , a tight-binding picture is illustrative. The bandwidth for interchain transport is directly proportional to t_c , while the effective mass for interchain transport is inversely proportional to t_c . However, for small t_c this band becomes unstable for electronic interactions V .^{4,14} The interchain charge transfer is typically $t_c \sim 0.01-0.1$ eV (Refs. 15,19 and 20) and $V = e^2 / (4\pi\epsilon_0\epsilon_B r)$, with r the separation between charges. For optimal doping of 1 charge per 4 monomers, the distance between charges r is a few nm and $V \approx 0.1$ eV. It shows that indeed t_c is of the order of the electron-electron interaction energy.

What could be expected for the carrier dynamics if t_c and V play a role in the MIT? Since at present theories incorporating both strong disorder and strong interactions are not available, we have to limit ourselves to the following necessarily qualitative discussion of what *might* be expected. When decreasing t_c , m^* increases (even for the most delocalized carriers in highly-ordered regions the overlapping π -electron clouds of adjacent chains lead to transfer integrals that are relatively small when compared to the common

three-dimensional electron systems) and it has even been suggested to diverge near the critical point.¹⁴ On the other hand, the density of delocalized states g vanishes near the MIT.^{4,14} This implies a strong increase of g/m^* and ω_p with increasing $E_F - E_c$ in qualitative agreement with our experimental findings, see Fig. 4. To our knowledge, a relation between g/m^* and distance to the MIT is not available. The divergence of m^* leads to a strongly decreasing free-carrier velocity $v \propto \sqrt{(E_F - E_c)/m^*}$ near the critical point. Since $\tau^{-1} \propto v$ and $\tau^{-1} \propto g$ as well,¹² we expect $\tau \propto g^{-1} v^{-1}$ to decrease strongly in the metallic regime. Note that now the decrease of τ not necessarily implies the counterintuitive shorter l in the metallic phase since v increases. Hence the unusual decrease of τ and increase of g/m^* with $E_F - E_c$ can be understood when the MIT involves an interplay between t_c and V .

How can we reconcile this picture with the well-established observations that structural disorder^{6,7} drives the MIT? The interchain π -electronic overlap t_c depends *exponentially* on separation and orientation of adjacent chain (segments) and is therefore particularly sensitive to the local ordering of polymer chains. Deviations from the optimal

packing make the allowed bandwidth exponentially narrow and the effective mass exponentially large. Due to this extreme sensitivity, a disorder-induced decrease of t_c with respect to V may be the dominant driving mechanism for the MIT instead of disorder-induced localization. We note that x-ray diffraction studies^{21–23} demonstrate that a high conductivity in PPy requires a close packing of adjacent pyrrole rings which should be favorable for t_c . The dependence of the MIT on pressure, which enhances t_c ,^{19,24} confirms this point of view.

In summary, we have studied the free-carrier dynamics in PPy-PF₆ near the MIT. The specific T -dependence of ω_p and τ can be reproduced by only two free parameters: $E_F - E_c$ and g/m^* . The decrease of τ in better conducting samples contradicts the conventional disorder-only models. We have argued that the found carrier dynamics in the vicinity of the MIT can be qualitatively explained when also the competition between electronic correlations and interchain charge transfer is considered, and where the value of the latter is strongly influenced by the amount of structural disorder.

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- ¹M.J. Hirsch, *Comments Condens. Matter Phys.* **13**, 249 (1987).
- ²P.W. Anderson, *Phys. Rev.* **109**, 1492 (1958).
- ³P.A. Lee and T.V. Ramakrishnan, *Rev. Mod. Phys.* **57**, 287 (1985).
- ⁴J. Hubbard, *Proc. R. Soc. London, Ser. A* **277**, 237 (1964).
- ⁵N.F. Mott and W.D. Twose, *Adv. Phys.* **10**, 107 (1961).
- ⁶C.O. Yoon, M. Reghu, D. Moses, and A.J. Heeger, *Phys. Rev. B* **49**, 10 851 (1994).
- ⁷R.S. Kohlman *et al.*, *Phys. Rev. Lett.* **78**, 3915 (1997).
- ⁸K. Lee, R. Menon, C.O. Yoon, and A.J. Heeger, *Phys. Rev. B* **52**, 4779 (1995).
- ⁹J. Joo *et al.*, *Phys. Rev. B* **57**, 9567 (1998).
- ¹⁰K. Lee *et al.*, *Phys. Rev. B* **61**, 1635 (2000).
- ¹¹T. Hagiwara, M. Hirasaka, K. Sato, and M. Yamaura, *Synth. Met.* **40**, 35 (1990).
- ¹²H.C.F. Martens *et al.*, *Phys. Rev. B* **63**, 125328 (2001).
- ¹³J.A. Reedijk, H.C.F. Martens, B.J.G. Smits, and H.B. Brom, *Rev. Sci. Instrum.* **71**, 478 (2000).
- ¹⁴N.H. March, *Electron Correlation in Molecules and Condensed*

Phases (Plenum Press, New York, 1996).

- ¹⁵R. Menon, C.O. Yoon, D. Moses, and A.J. Heeger, *Handbook of Conducting Polymers, Second Edition* (Marcel Dekker, New York, 1998).
- ¹⁶T.G. Castner, *Phys. Rev. Lett.* **84**, 1539 (2000).
- ¹⁷A. Raghunathan *et al.*, *Phys. Rev. B* **58**, R15 955 (1998).
- ¹⁸Although, effectively, interchain transport will involve some intrachain transport as well, only for $\hbar \omega > t_c$ intrachain transport is expected to dominate.
- ¹⁹V. Vescoli *et al.*, *Science* **281**, 1181 (1998).
- ²⁰M. Paulsson and S. Stafström, *Phys. Rev. B* **60**, 7939 (1999).
- ²¹Y. Nogami, J.-P. Pouget, and T. Ishiguro, *Synth. Met.* **62**, 257 (1994).
- ²²J.H. Kim *et al.*, *Synth. Met.* **84**, 71 (1997); *ibid.* **84**, 737 (1997).
- ²³M.J. Vinokur, *Handbook of Conducting Polymers, Second Edition* (Marcel Dekker, New York, 1998).
- ²⁴K. Väkiparta *et al.*, *Phys. Rev. B* **47**, 9977 (1993).