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Metallic state in disordered quasi-one-dimensional conductors

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The metallic state in conjugated polymers and single-walled carbon nanotubes is studied by dielectric spectroscopy (8–600 GHz). We have found an intriguing correlation between scattering time (τ) and plasma frequency (ω_p): $\tau \propto \omega_p^{-1.3}$. This relation conflicts with the usually applied models that only consider disorder. Based on the observed parallels with doped semiconductors, we argue that the interchain coupling $t_\perp$ plays a role comparable to the doping level and that the unusual free-carrier dynamics in the metallic state can be explained when including the role of $t_\perp$ in the conventional models.

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The metal-insulator transition (MIT) in disordered quasi-one-dimensional (1D) conducting polymers and single-walled carbon nanotubes is generally accepted to be disorder-driven, but its exact nature is under severe debate. Many authors claim the presence of a ''heterogeneous'' state in which the relevant disorder length scale is large compared to the electronic correlation length. In this case, the MIT corresponds to a percolation transition of metallic islands embedded in an amorphous matrix.[1–3] Other studies suggest that the MIT is of the Anderson type with ''homogeneous'' disorder occurring on length scales equal or less than the electronic correlation length.[4,5] Then, extended and localized states are separated in energy by the mobility edge, and the MIT occurs when the Fermi level crosses this mobility edge.

We have studied charge transport in polyaniline, polypyrrole, and single-walled carbon nanotubes by means of dielectric spectroscopy in the range 8–600 GHz ($0.27-20$ cm^{-1},$0.033-2.5$ meV).[6] This technique covers both the microwave and far-infrared regime, and does not rely on Kramers-Kronig analyses.[6] Compared to conventional metals, the plasma frequencies (ω_p) are very low and the scattering times (τ) anomalously long. We point out an intriguing correlation between ω_p and τ, which shows that disorder alone, ''heterogeneous'' or ''homogeneous,'' is insufficient to explain the unusual carrier dynamics. Uncompensated doped semiconductors reveal similar unusual carrier dynamics, and we conjecture that in the disordered quasi-1D conductors the interchain coupling plays a role analogous to doping level in electronic systems where disorder and/or electronic correlations lead to carrier localization.

Preparation details of the materials studied are given elsewhere.[4,7,8] The temperature-dependent dc conductivity is shown in Fig. 1. Both single-walled carbon nanotubes and polypyrrole have a finite dc conductivity down to the lowest temperatures, indicating a metallic state. The dc conductivity of polyaniline vanishes when cooling, characteristic of an insulating phase. Clearly, all samples are on the boundary of the MIT.

Figure 2 presents the results of the dielectric experiments. For all samples, at low frequency the dielectric constant ε is negative. Such behavior is expected for delocalized-carrier transport, and agrees with the results of Kohlman and co-workers.[1] The conductivity σ reveals only a weak frequency dependence. For conventional metals, the frequency ($\omega = 2\pi f$) dependence of the complex conductivity, $\sigma^* = \sigma + i\omega\varepsilon_0\varepsilon$ (ε_0 vacuum permittivity), is well explained in terms of the Drude free-electron model:

$$\sigma^*(\omega) = \frac{\varepsilon_0 \omega_p^2 \tau}{1 + i\omega\tau} \tag{1}$$

with τ being the scattering time and

$$\omega_p = \sqrt{ne^2/(\varepsilon_0 m^*)} \tag{2}$$

the unscreened plasma frequency, n is the free-carrier density, e is the electronic charge, and m^* is the effective mass. According to Eq. (1), for $\omega\tau < 1$, ε is negative and σ is

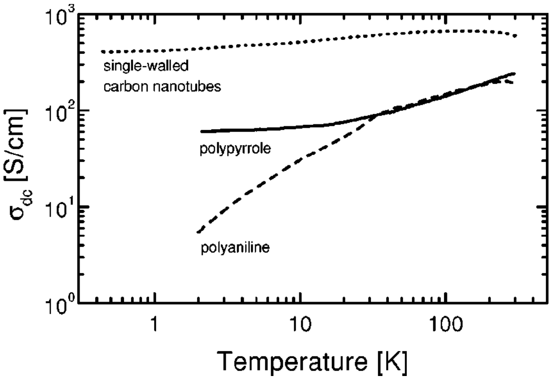

FIG. 1. Temperature-dependent dc conductivity of three disordered quasi-1D systems. All samples are close to the MIT. Below 10 K the dc conductivities of polypyrrole and single-walled carbon nanotubes are almost temperature independent implying a nonzero conductivity at zero Kelvin as expected for a metal. The dc conductivity of polyaniline vanishes when cooling, indicating that this sample is on the insulating side of the MIT.

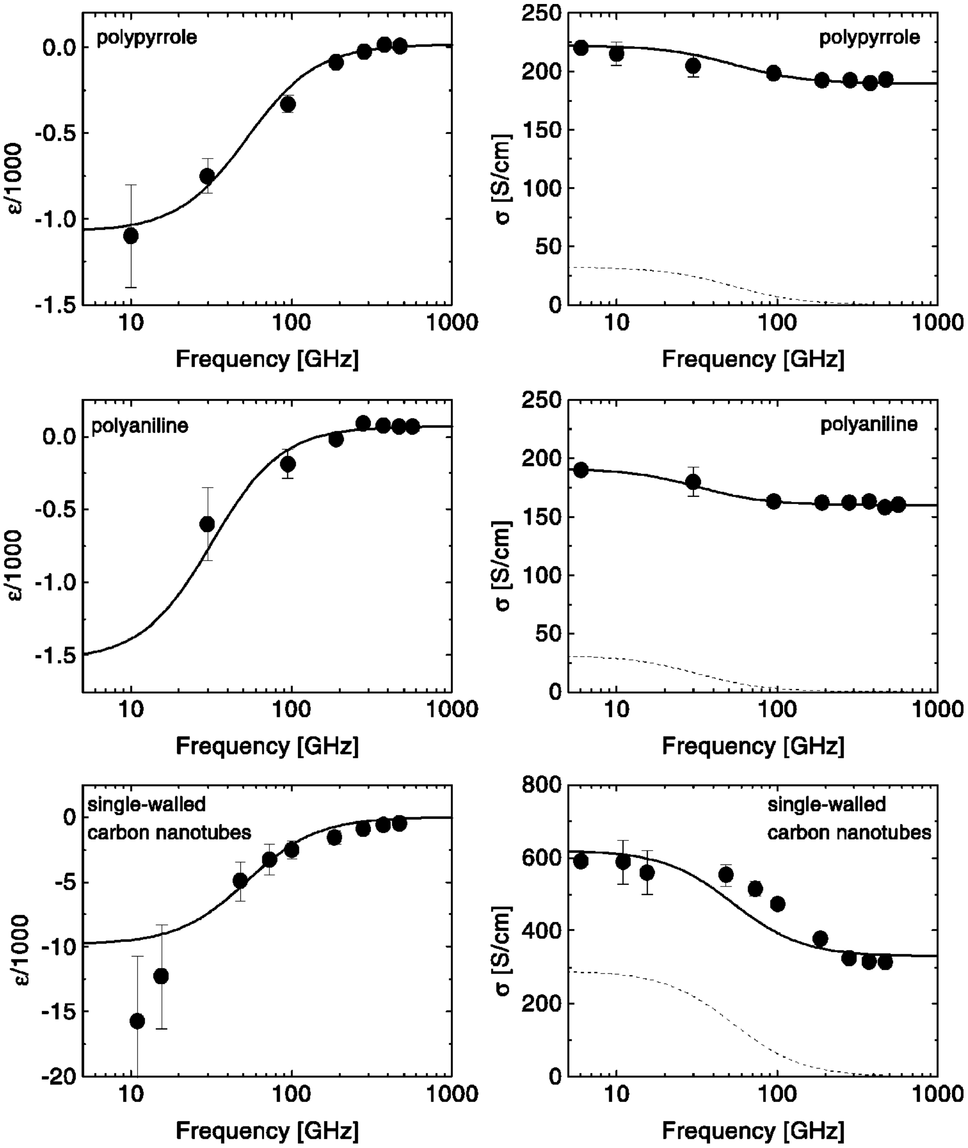

FIG. 2. Room-temperature dielectric function (left) and conductivity (right) as a function of frequency for polypyrrole, polyaniline, and single-walled carbon nanotubes, respectively. In view of the logarithmic scale, the value of σ_{dc} is plotted at $f=6$ GHz. The drawn lines are fits to the data using the Drude equation with an extra (frequency independent) background conductivity and dielectric constant. The dielectric data are dominated by the free-carrier response. However, the free-carrier contribution to the conductivity (dashed lines) is less than 50%.

frequency independent. For $\omega\tau>1$, σ drops to zero, while ε increases and eventually becomes positive above ω_p. For normal metals $\omega_p\sim1-10$ eV, and $\tau\sim10^{-14}$ s.[9] However, contrary to Eq. (1), σ of the materials studied here does not drop to zero but reaches a ''plateau'' at high frequency, indicating an additional absorption mechanism. By incorporating a frequency-independent background conductivity σ_b and dielectric constant ε_b in Eq. (1), the data can be excellently reproduced, see the solid lines in Fig. 2. From the fits we find for, respectively, polypyrrole, polyaniline, and single-walled carbon nanotubes: ω_p (meV)$=7.3\pm0.5$, 6 ± 1 and 22 ± 7; τ(ps)$=3\pm0.5$, 5 ± 1 and 3 ± 1.5; $\varepsilon_b=18\pm1$, 70 ± 10 and 0 ± 500; σ_b (S/cm)$=190\pm10$, 160 ± 10, and 370 ± 50. The free-carrier response of polyaniline shows that, for a sample just on the insulating side of the MIT, extended states become thermally occupied at finite temperature.[10]

Figure 3 displays the room-temperature Drude parameters of disordered quasi-1D conductors studied here, and also includes values of ω_p and τ reported by Kohlman and coworkers.[1] For comparison, Drude parameters of conventional metals,[9] intrachain conduction in crystalline 1D conductors,[11,12] graphite,[13] and uncompensated doped semiconductors[14–16] are included as well. The conducting polymers, represented by the black dots, reveal a remarkable empirical correlation $\tau\propto\omega_p^{-1.3}$. Comparable trends are observed for the doped semiconductors. The open symbols correspond to the ''second'' plasma frequency observed in conducting polymers,[1,5] and single-walled carbon nanotubes.[17] The Drude parameters of conducting polymers and single-walled carbon nanotubes are very unlike those of conventional metals and crystalline 1D conductors.

The unusual carrier dynamics in conducting polymers has been argued to indicate a ''heterogeneous'' metallic state.[1] In this model, upon decreasing disorder, the fraction of metallic regions increases and this should increase the low-energy ω_p.[1] However, the intrinsic conductive properties of metallic islands are not expected to depend on the concentration of such islands. For instance, in a bulk metal ε is zero at the plasma frequency. Based on effective-medium calculations, Stroud[18,19] showed that the zero in ε at $\omega=\omega_p$ persists in a metal-insulator-composite for metal fractions above the per-

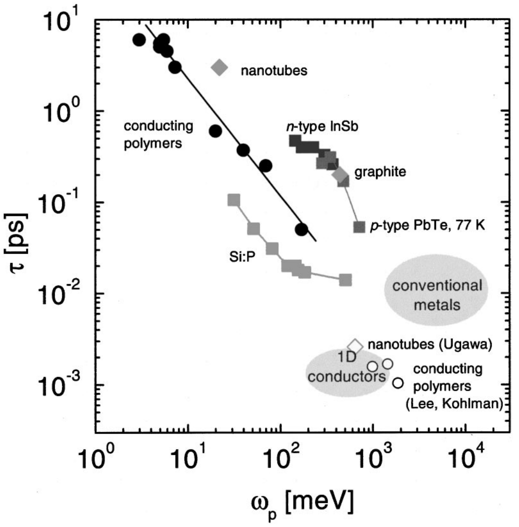

FIG. 3. Room-temperature values of the Drude parameters τ and ω_p describing the metallic state in doped conjugated polymers and single-walled carbon nanotubes. For comparison the typical values of conventional metals, crystalline 1D conductors, graphite, and several doped semiconductors are indicated. In our view, the closed symbols correspond to the free-carrier response of 3D extended states, while the open symbols can be attributed to on-chain (1D) motion of charge carriers. The empirical correlation $\tau \propto \omega_p^{-1.3}$ for the conducting polymers, seems to extrapolate to parameter ranges of conventional conductors.

colation threshold, hence the plasma frequencies in the bulk and composite are the same. This is a natural consequence of the fact that ω_p only depends on the carrier density inside the percolating metallic path, and not on the free-carrier density in the total volume of the composite material. Indeed, recent experiments on thin heterogeneous Pb films demonstrated the presence of only a single ω_p, which is independent of the fraction of Pb and almost equal to the plasma frequency of bulk lead.[20] In contrast, the low-energy plasma frequency in conducting polymers shows an increase of almost two orders of magnitude, see Fig. 3, at variance with the behavior expected for a percolating metallic network. Also, in terms of the heterogeneous model, Fig. 3 would imply that an increase of the fraction of metallic islands enhances the carrier scattering, which seems unlikely.

Alternatively, it has been proposed that conducting polymers should be viewed as conventional ''homogeneously'' disordered metals for which the Anderson theory applies.[4,5] The low ω_p would imply that only a fraction of carriers occupy states above the mobility edge. However, the observed anomalously long τ's in disordered quasi-1D systems do not support the presence of a strongly disordered metal. Moreover, a decrease of τ with increasing ω_p, apparently reflecting decreasing disorder, seems physically impossible. Hence, we conclude that both the ''homogeneous'' and ''heterogeneous'' disorder models, which are commonly applied to describe the MIT in these systems, are unable to explain the empirical correlation between ω_p and τ.

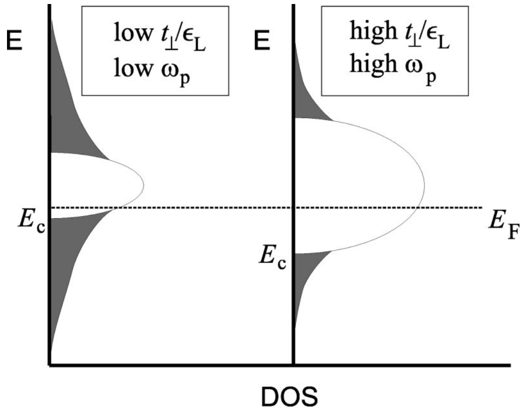

FIG. 4. Schematic drawing of the density of states (DOS) in disordered quasi-1D conductors as a function of $t_\perp$ (interchain overlap) and ϵ_L (energy scale of localization mechanism). Localized states are indicated in gray, extended states are indicated in white. At constant doping level, when increasing the ratio $t_\perp/\epsilon_L$ extended states are formed at the expense of localized states, which gives a larger free-carrier density n and consequently a larger ω_p. The metallic state only occurs when E_F lies in the region of extended states, which requires a high doping level together with large enough ratio $t_\perp/\epsilon_L$.

Figure 3 demonstrates that apart from conducting polymers, the Drude parameters of uncompensated doped semiconductors follow similar relations. This surprising result can provide an alternative viewpoint on the apparently unusual delocalized carrier transport in disordered quasi-1D systems as discussed below. In heavily doped semiconductors, at $T=300$ K all doped carriers participate in the delocalized transport; the increase of ω_p simply results from an increase of doping level. Since typically $n_{\text{doped}} \sim 10^{23} - 10^{25}$ m^{-3},[14–16] the low ω_p's reflect the low band-filling. In the optimally doped conducting polymers studied here, the doping level is not varied and therefore a different mechanism must lead to the two orders of magnitude change in ω_p. For these systems, $n_{\text{doped}} \sim 10^{27}$ m^{-3}, the band-filling is high and one expects $\omega_p \sim 1$ eV. However, the observed plasma frequencies are orders of magnitude lower, which implies that only a fraction of the carriers are delocalized: $n \ll n_{\text{doped}}$. Indeed, in truly 1D systems both disorder and electronic correlation lead to strongly localized carriers and the metallic state is suppressed. Clearly, to obtain extended states, interchain charge transfer is a prerequisite. This is an essential condition, regardless of the morphology being heterogeneous or homogeneous, for the formation of the metallic state. The competition between the energy scale ϵ_L associated with the dominant localization mechanism (for instance disorder or interactions[21]) and the interchain charge-transfer intergral $t_\perp$ governs the density of such delocalized states. As is schematically depicted in Fig. 4, even if n_{doped} remains constant, n (and hence ω_p) will increase when $t_\perp/\epsilon_L$ increases: the parameter $t_\perp/\epsilon_L$ plays a role comparable to doping level. In order to achieve a truly metallic state, both n_{doped} and $t_\perp/\epsilon_L$ must be high enough to have E_F in the region of delocalized states, which explains why the metallic state only occurs in highly doped polymers.

The correlation between ω_p and τ demonstrated in Fig. 3 suggests that the anomalous values of these parameters relate to a common mechanism. In general, the carrier's scattering probability is amongst other factors proportional to the density of final states it can reach: if there are no states available it cannot scatter. Therefore, the anomalously long τ's in conducting polymers and carbon nanotubes also could simply reflect the low density of delocalized states. This naturally explains the interrelation between ω_p and τ: when the density of delocalized states increases a larger n and therefore larger ω_p results; at the same time the enhanced probability for scattering will reduce τ.

To quantify the above discussion, we use Eq. (2) and take as a typical density of states $g \sim 1$ state/(eV ring)[1] and $\omega_p \sim 30$ meV. As an estimate of n we consider a weakly metallic sample for which $E_F - E_c < k_B T$, so $n \approx k_B T g$, giving $n \sim 10^{25}$ m^{-3} and $m^* \sim 15 m_e$ (m_e electronic mass). Alternatively, when using a free-electron approximation, we find $n \sim 10^{24} - 10^{25}$ m^{-3} and $m^* \sim 10 m_e$. As expected, $n \ll n_{\text{doped}}$. The high m^* agrees with a low interchain overlap, which gives narrow electronic bands and hence heavy masses. From the derived m^* and n we estimate $E_F - E_c$ to be only a few meV. Since $k_B T \gg E_F - E_c$ the delocalized carriers obey classical statistics. In this case the average velocity $\overline{v} \approx \sqrt{k_B T / m^*} \approx 2 \times 10^4$ m/s. Since $\tau \sim 0.5$ ps for $\omega_p \sim 30$ meV, we find a mean free path $l \sim 10$ nm.

In both single-walled carbon nanotubes and conducting polymers a second plasma frequency has been reported around 1 eV, with $\tau \sim 10^{-15}$ s.[1,5,17] These values match the on-chain parameters in crystalline 1D conductors, and could reflect the motion of the majority of carriers which are not 3D delocalized but confined to 1D chains. Indeed, this corroborates our suggestion that coherent interchain motion of carriers only occurs for the small fraction of carriers governed by $t_\perp$, see Fig. 4. Lee *et al.* calculated that the 1D-localized carriers contribute 50−70% to the total dc conductivity,[5] in agreement with σ_b in the fits of the GHz response (Fig. 2).

Finally, we address the role of disorder. It is well established that the formation of a metallic state in conducting polymers requires careful preparation in order to minimize structural disorder. In the model proposed here the role of structural (dis)order can be naturally explained. Independent of the nature of disorder (homogeneous or heterogeneous), a decrease of the structural disorder merely reflects that locally polymer chains are better packed. This will favor interchain interactions and, at the same time, reduce the strength of the random potential experienced by the charge carriers. Both effects enhance the metallic state. Whether or not this metallic state is heterogeneous, depends on the detailed morphology of the polymer, but it is clear that a full understanding of the conductive properties of these systems requires $t_\perp$ to be incorporated in the existing models based on disorder only.

In summary, the empirical correlation between τ and ω_p for both conducting polymers and doped semiconductors as demonstrated in Fig. 3, is an important result of this work. It shows that the unusual carrier dynamics, i.e., anomalously low ω_p's and long τ's, in these conductors can be consistently explained in terms of a marginally metallic system with a low density of delocalized states. In polymers and nanotubes, the competition between interchain charge transfer and localization onto 1D chains plays a role comparable to that of doping level. Extrapolating the empirical correlation suggests the possibility of further improvement of the conductive properties of these materials, though beyond those of conventional metals seems doubtful.

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