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Universal Scaling in Highly Doped Conducting Polymer Films

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Electrical transport of a highly doped disordered conducting polymer, viz. poly-3,4-ethylenedioxythiophene stabilized with poly-4-styrenesulphonic acid, is investigated as a function of bias and temperature. The transport shows universal power-law scaling with both bias and temperature. All measurements constitute a single universal curve, and the complete $J(V, T)$ characteristics are described by a single equation. We relate this scaling to dissipative tunneling processes, such as Coulomb blockade.

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The first highly conducting organic polymer, chemically doped polyacetylene, was reported in 1977 [1]. A fundamental and still unresolved question is the nature of the charge transport in conjugated polymers. Since interactions between monomers are covalent, leading to strong orbital overlap and delocalization over the π -conjugated system, conjugated polymers can be regarded as one-dimensional semiconductors. On the other hand, disorder due to kinks, cross-links, and impurities will disrupt the π system, and transport will be governed by hopping between conjugated parts of one polymer chain or neighboring chains, resembling a three-dimensional semiconductor. To describe the properties of standard three-dimensional conductors, the Fermi liquid theory is widely used. Introducing disorder in a Fermi liquid induces localization, and consequently electrical transport occurs by hopping of charge carriers at the Fermi level. For many doped, disordered organic polymers, the conductivity was reported to follow a stretched exponential temperature dependence: $\sigma \propto \exp[-(1/T)^\nu]$ [2]. The reported values for the exponent ν suggest so-called variable range hopping in one to three dimensions: $\nu = 1/(D + 1)$, where D , the number of dimensions, varies between 1 and 3 [3]. In one-dimensional systems, however, quantum confinement amplifies Coulomb interactions between electrons, and the Luttinger liquid theory needs to be applied [4]. Typical for the Luttinger liquid theory is that the dispersion relation near the Fermi energy is approximated as both linear and continuous. This assumption is valid when high-energy excitations can be disregarded and when the one-dimensional lattice is semi-infinite. The combination of a linear dispersion and Coulomb interaction results in a power-law density of states that vanishes at the Fermi level. Hence, tunneling into a Luttinger liquid yields power-law relations with both temperature and voltage, more exactly, $J \propto T^\alpha$ at low voltages ($kT \gg eV$) and

$J \propto V^\beta$ at low temperatures ($eV \gg kT$), with $\beta = \alpha + 1$. Furthermore, when the scaled current density $J/T^{1+\alpha}$ is plotted as a function of eV/kT , a universal curve is obtained described by [5–7]

$$J = J_0 T^{1+\alpha} \sinh\left(\gamma \frac{eV}{kT}\right) \left| \Gamma\left(1 + \frac{\alpha}{2} + i\gamma \frac{eV}{\pi kT}\right) \right|^2, \quad (1)$$

where the parameter α is derived from the measurements, J_0 and γ are two fit parameters, e is the elementary charge, k is the Boltzmann constant, and Γ is the Gamma function. The fit parameter γ^{-1} has been related to the number of tunnel barriers between the contacts and determines a crossover from Ohmic behavior to a power-law dependence.

It has recently been reported that Eq. (1) describes the charge transport of the conjugated polymer poly(2,5-bis-(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) in high carrier density field-effect transistors and in electrochemically doped films [8]. Density functional theory calculations have classified PBTTT as a quasi-one-dimensional system [9]. Supported by the fit of Eq. (1) and the calculated electrical anisotropy, the scaling of the electrical transport has been interpreted as a fingerprint of Luttinger liquid behavior originating from one-dimensional transport in conjugated polymers [8,10].

To address whether one-dimensionality is a prerequisite for the power-law scaling, we studied the charge transport in poly-3,4-ethylenedioxythiophene stabilized with poly-4-styrenesulphonic acid (PEDOT:PSS). This complex is a mixture of doped PEDOT stabilized with PSS. Thin films can be spin coated from waterborne lattices and exhibit conductivities up to about 1000 S/cm. Scanning tunneling and electron microscopy studies have shown that the microstructure consists of spherical grains on the order of 20–50 nm [11,12]. The individual grains have a PEDOT-rich core and a PSS-rich shell [12]. Therefore, PEDOT:PSS

is a three-dimensional disordered electronic system and a model compound for highly doped conducting polymers. Previously, the conductivity of PEDOT:PSS was reported to follow a stretched exponential temperature dependence [13–16]. However, contrary to the stretched exponential temperature dependence, a few reports have also shown a power-law dependence [14,17,18]. The bias dependence of these measurements has not been reported. Here we present a detailed analysis of the electrical transport as a function of both bias and temperature.

To test the validity of Eq. (1), a crossover from Ohmic transport to a power-law dependence has to be observed. This implies a relatively large value of γ that can be realized only with small electrode spacing, on the order of 100 nm. To this end we measure the transport transversal through PEDOT:PSS thin films fabricated in so-called large-area molecular junctions, as shown in Fig. 1. On a gold bottom electrode circular via holes of 1–50 μm in diameter are lithographically defined in photoresist. PEDOT:PSS is spin coated yielding a thickness of ~ 90 nm and, finally, a gold top electrode is evaporated and patterned to prevent cross talk. Stable and reproducible junctions were obtained. The current through the junctions scaled with the lateral dimensions with a small standard deviation [19–21].

The current density voltage (J - V) characteristics averaged over 8 PEDOT:PSS junctions are presented as a function of temperature in Fig. 2. The bias was varied between 0 and 0.5 V, and the temperature was varied between 25 and 300 K. The transport characteristics are symmetric for negative and positive bias. At room

temperature, the transport is Ohmic up to the applied bias of 0.5 V. At lower temperatures, the current density decreases and the transport deviates from Ohmic behavior. To magnify the nonlinearity, measurements at higher bias are required. However, at room temperature the junctions break down at higher bias due to hydrolysis of remaining water in the PEDOT:PSS layer [21]. To circumvent the breakdown, pulse measurements were applied. At low temperature and with a low duty cycle the transport could be measured up to high biases of 3 V, while at higher temperatures hydrolysis still hampered the measurements. The current density voltage (J - V) characteristics up to 3 V are presented as a function of temperature between 25 and 100 K in Fig. 3. At low bias the current density decreases with decreasing temperature. At higher biases the temperature dependence disappears.

To analyze the electrical transport, the current density as a function of temperature is plotted on a double logarithmic scale. The inset in Fig. 3 shows that straight lines are obtained, indicating a power-law dependence of current density on temperature. The slope depends on the applied bias. Extrapolating the value of the slope to 0 V bias, where $kT \gg eV$, yields $J \propto T^\alpha$ with $\alpha = 1.25$. With this fixed value of α we calculated at each temperature the scaled current density $J/T^{1+\alpha}$. Figure 4 shows the scaled current density as a function of the dimensionless parameter eV/kT . Both dc measurements at low bias and pulse measurements at high applied bias are included. Varying the temperature between 25 and 300 K and the bias between 0 and 3 V leads to a change in the parameter eV/kT over 4 orders of magnitude. The corresponding scaled current density then varies over 6 orders of magnitude. Figure 4 nevertheless shows that even over this wide

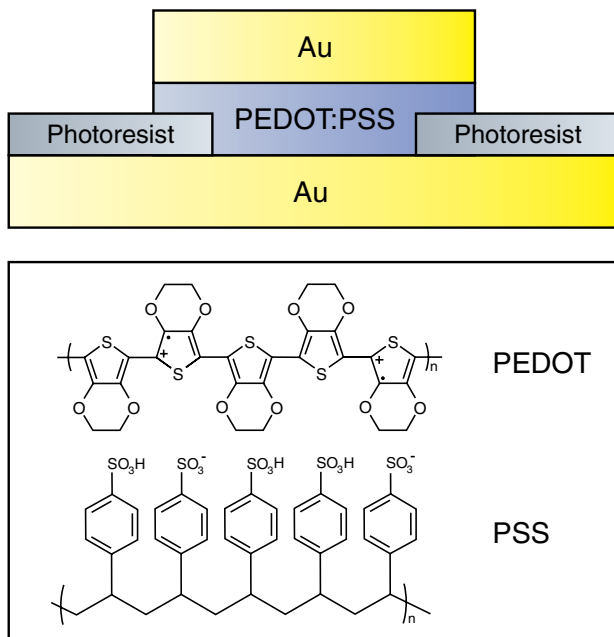


FIG. 1 (color online). Device layout. Schematic representation of the large-area molecular junctions and the chemical structure of PEDOT:PSS.

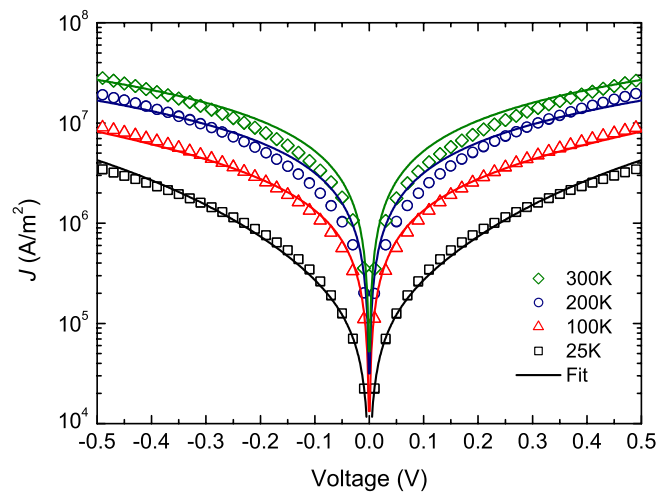


FIG. 2 (color online). Electrical transport at low bias. J - V characteristics of the PEDOT:PSS junctions up to 0.5 V bias at temperatures between 25 and 300 K. The current density is averaged over 8 devices with a device diameter between 5 and 50 μm . The solid curves stem from the universal curve calculated by using Eq. (1).

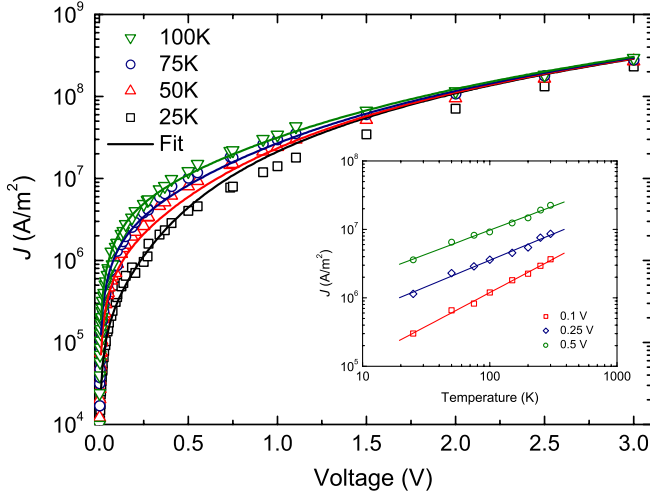


FIG. 3 (color online). Electrical transport at high bias. J - V characteristics of the PEDOT:PSS junctions up to 3 V bias at temperatures between 25 and 100 K. The current density is averaged over 6 devices with a device diameter of 4 and 5 μm . The solid curves stem from the same universal curve calculated by using Eq. (1). The inset shows the J - T characteristics on a double logarithmic scale.

parameter space a universal dependence is obtained. The solid curve in Fig. 4 is calculated by using Eq. (1). Perfect agreement is obtained by using the fit parameters γ of 0.025 and J_0 of 200 A/m^2 . The quality of the fit is illustrated by recalculating the discrete $J(V, T)$ characteristics. The solid curves in Figs. 2 and 3 are computed and

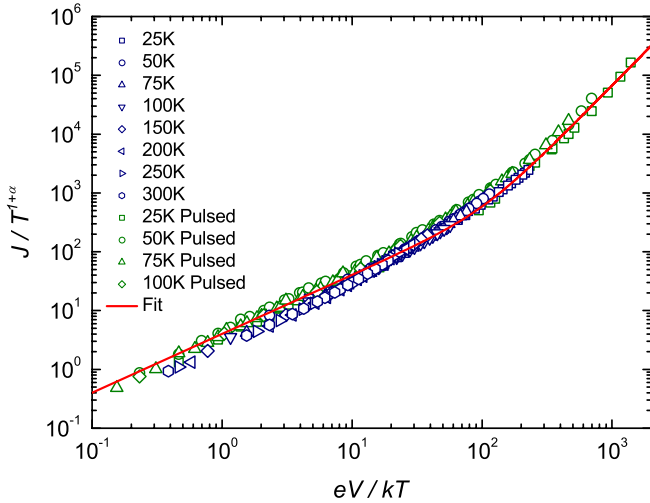


FIG. 4 (color online). Scaling of electrical transport. The scaled current density as a function of the dimensionless parameter eV/kT . Both dc measurements at low bias (Fig. 2) and pulse measurements at high applied bias (Fig. 3) are included. The solid curve is calculated by using Eq. (1) with fit constants $\gamma = 0.025$ and $J_0 = 200 \text{ A}/\text{m}^2$. The solid curves of Figs. 2 and 3 are generated from this fit.

demonstrate that with only two parameters the complete $J(V, T)$ curves can be described.

Figure 4 shows that for small values of eV/kT the slope of the scaled current density is unity. This Ohmic behavior implies that at a fixed, low bias the current density follows a power-law dependence on temperature as $J \propto T^\alpha$ with $\alpha = 1.25$. For values of eV/kT much larger than unity, the slope of the scaled current density becomes about 2.25. This implies that at a fixed, low temperature the current density follows a power-law dependence on bias as $J \propto V^\beta$ with $\beta = 2.25$. The crossover from linear to superlinear behavior is dominated by the value of the parameter γ . The parameter J_0 is a multiplication constant.

Equation (1), which completely describes the $J(V, T)$ characteristics, has been shown to hold for a Luttinger liquid. However, the reverse is not necessarily true; i.e., if the $J(V, T)$ characteristics can be described by Eq. (1), this does not automatically imply that one is dealing with a Luttinger liquid. In fact, Eq. (1) was originally derived for dissipative tunneling in a biased double-well quantum system where the electron tunnels between the two wells [6,7]. Dissipative coupling was provided by an (unspecified) external heat bath. Although Luttinger liquid behavior is not a necessary condition for Eq. (1), this equation has since been used as a direct proof of Luttinger liquid behavior [5]. Given this background, we note again that PEDOT:PSS is a disordered conducting polymer; the microstructure of thin films consists of spherical amorphous grains [11,12]. Furthermore, the conjugation of PEDOT chains is too short to form a semi-infinite one-dimensional lattice needed for a Luttinger liquid. Hence, PEDOT:PSS is effectively a three-dimensional electronic system and can therefore not be regarded as a Luttinger liquid. Nevertheless, we observe scaling behavior.

Another physical origin related to three-dimensional electronic systems is thus responsible for the scaling. In general, the tunneling rate at an energy E is determined by a convolution of the tunnel probability $P(E)$ and the density of states $\rho(E)$. The observed scaling can thus originate from power-law scaling of either $P(E)$ or $\rho(E)$ [22]. Power-law scaling of $\rho(E)$ arises naturally in a Luttinger liquid because of the linear dispersion relation. Scaling of $P(E)$ arises in the general dissipative tunneling models due to coupling of the system with an (unspecified) environment [6,7]. Additional effort to specify dissipation has resulted in the theoretical description of systems where unconventional Coulomb blockade mechanisms yield power-law behavior. The most prominent is so-called environmental Coulomb blockade in ultrasmall tunnel junctions [23,24], while also arrays of relatively strongly coupled quantum dots [25,26] and nonconventional tunneling between disordered conductors [27–29] produce similar results. The specific models yield power-law behavior that can hardly be distinguished from Luttinger liquid behavior [22,30,31].

Weak Coulomb blockade is a viable option to explain the scaling behavior in PEDOT:PSS [26], since thin films consist of relatively strongly coupled PEDOT grains [32]. Coulomb blockade is, however, not immediately expected for PBTBT because of the semicrystalline microstructure of the films. Therefore, a general origin of the universal scaling cannot be unambiguously determined from the present experimental efforts.

In conclusion, we have shown that the electrical transport of PEDOT:PSS junctions as a function of both temperature and bias can be described over a wide parameter space by a single equation with only two fit parameters. A similar scaling with temperature and bias has previously been reported for the highly doped conducting polymer PBTBT and has been interpreted as a signature of one-dimensional Luttinger liquid behavior. PEDOT:PSS, however, cannot be regarded as a one-dimensional electronic system. The scaling can be due to dissipative tunneling such as environmental Coulomb blockade, but the origin cannot unambiguously be assigned. Scaling nevertheless appears to be general for highly doped polymer systems and opens new opportunities for understanding the charge transport in these materials.

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- [32] The size of the PEDOT grains is consistent with the weak Coulomb blockade regime at elevated temperatures. For this regime, it is required that the grain-to-grain resistance $R \ll h/2e^2$ (relatively strongly coupled islands) and that $kT \lesssim \hbar/RC = (e^2/2C)(R_0/R)$ with $R_0 = 2\hbar/e^2$. Note that $R_0/R \gg 1$ via the first requirement. We estimate the total capacitance for a 30 nm PEDOT grain at 10 aF, resulting in a charging energy $E_c = e^2/2C = 8$ meV. Hence for moderate values of R_0/R the weak Coulomb blockade regime is still valid at room temperature.