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$f^{-\gamma}$ current fluctuations in organic semiconductors: evidence for percolation

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Abstract. The $f^{-\gamma}$ sloped current noise power spectra, observed in organic semiconductors, have been interpreted within a *variable range hopping* mechanism of the fluctuations. The relative current noise power spectral density $\mathcal{S}(f) = S_I(f)/I^2$ exhibits a maximum at the *trap-filling transition* between the *ohmic* and the *space-charge-limited-current* regime [Phys. Rev. Lett. **95**, 236601 (2005)]. Here, we discuss the electronic conditions determining the crossover from ohmic to space-charge-limited transport. These arguments shed light on the need to adopt a *percolative* fluctuation picture to account for the competition between insulating and conductive phases coexisting at the *transition*, where small changes in the external bias lead to dramatic effects in the fluctuations.

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$f^{-\gamma}$ noise is an ubiquitous phenomenon observed in many systems [1]. In spite of the intense research effort, a general agreement on the origin of the $f^{-\gamma}$ noise and the information, carried by it about the underlying microscopic processes, has still to be achieved. In homogeneous conductors, the relative spectral density of the $f^{-\gamma}$ noise is independent of the voltage V when the Ohm law is obeyed. Furthermore, under the same assumptions, an increase (decrease) of the free charge carrier density n results in a monotonic decrease (increase) of the relative fluctuations. The relative noise power spectral density of the current $S_I(f)/I^2$, of the voltage $S_V(f)/V^2$, of the conductance $S_G(f)/G^2$ and of the charge carrier density $S_n(f)/n^2$ are indeed related by the following identities:

$$\mathcal{S}(f) = \frac{S_I(f)}{I^2} = \frac{S_V(f)}{V^2} = \frac{S_G(f)}{G^2} = \frac{S_n(f)}{n^2}. \quad (1)$$

Under the assumption of Poisson distributed fluctuations of the free charge carrier density n, it is $\langle \delta n^2 \rangle \propto n$ and the relationship (1) can be written as

$$\mathcal{S} \propto \frac{1}{n} f^{-\gamma}. \quad (2)$$

This simple proportionality fails to apply to inhomogeneous condensed matter systems maintained away from thermal equilibrium by an external excitation. The application of an electric, magnetic or photon field, due the diverse conductive properties of the coexisting phases and interfaces, causes the current paths to evolve spatiotemporally with respect to quasiequilibrium conditions. Similar phenomena occur in ferroelectrics, polymers and copolymers, superconductors and magnetic semiconductors, island-like metallic films, carbon-wax mixtures, polycrystalline semiconductors only to mention a few examples [2]. The common feature shared by these systems is the transformation undergone by the conduction patterns upon variation of a control parameter in an otherwise quasi-homogeneous structure. The modification of the conduction patterns upon an external bias results in a current flow occurring through a mixed-phase percolation process arising from a variable-strength competition between multiphase metallic and insulating components. Due to the strong localization and electron/hole interaction within the disordered lattice, the transport in such systems is characterized by phenomena as variable-range-hopping and polaronic effects. Both the amplitude and the spectral characteristics of the noise are extremely sensitive to the dynamics of the current paths upon the external excitation, current fluctuations have been demonstrated to be helpful when the electronic properties of inhomogeneous systems have to be probed [3–13]. As a rule, the behavior expected on the basis of equation (1) for homogeneous conductors, is not observed in inhomogeneous

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systems. Relative noise power spectral densities changing with the bias have been indeed reported. Furthermore, the $1/n$ dependence of the relative noise lacks to occur when the charge carrier density n is changed. $1/n$ deviations are for example obtained when polycrystalline photosensitive materials are irradiated. The photon flux- preferentially and disorderly — increases the conductivity of the regions where photosensitive defects are located, resulting in the formation of coexisting paths having different conductivities [4,5]. Another feature often observed in inhomogeneous systems is the non-gaussianity of the noise traces. All the mentioned issues are diverse aspects of an unique problem: the charge carrier transport takes places across narrow conductive paths, with a volume which is only a small part of the whole conductor and with always less "fluctuators" involved in the stochastic process.

$f^{-\gamma}$ fluctuations have been recently observed in thin films of pentacene and tetracene. Pentacene and tetracene are small-weight organic molecules formed respectively by five, $C_{22}H_{14}$, and four, $C_{18}H_{12}$, benzene-like rings [6]. The study of noise in organic insulators is interesting at least for two reasons: (i) a complete understanding of the mechanisms underlying the charge carrier transport in organic small chain and polymers has not yet been fulfilled and still many unsolved issues remain; (ii) the deployment of organic and polymeric materials in the electronic industry requires a detailed insight into the dynamics other than into the time-averaged properties of the charge carrier transport [14–24].

We have reported that the relative power spectral density $\mathcal{S}(f)$ observed in polycrystalline polyacenes is consistent with steady fluctuations of thermally generated and of injected charge carriers, respectively in *ohmic* and in *space-charge-limited-current* (SCLC) regime. The relative noise suddenly increases at the *trap filling* region at intermediate voltage. The peak has been estimated within a simple percolation model of the fluctuations as a consequence of the imbalance between empty and filled traps. The *ohmic* transport is governed by thermally activated charge carriers with the deep traps almost completely empty. In SCLC regime, the transport is governed by the injected charge carriers, controlled by space-charge, with the deep traps almost completely filled. The intermediate voltage region, the *trap-filling transition* (TFT), is characterized by the coexistence of a conductive and an insulating phase, corresponding respectively to the empty and filled traps. The system can be viewed as a two-components continuum percolative medium. The material, initially in the quasi-homogeneous ohmic phase, becomes populated by insulating sites as the voltage increases. The conductivity patches become extremely intricate owing to the inhomogeneous distribution of trapping centers, whose occupancy randomly evolves as the Fermi level moves through the trap level. The system is in a strongly disordered state, due to the nucleation of insulating patterns inside the conductive medium. The relative noise intensity $\mathcal{S}(f)$ of the system undergoing the trap-filling-transition exceeds that of the same system when one of the two phases prevails. The increase of fluctuations has its origin in the greatly disordered distribution of local fields compared to the almost uniform distribution characterizing the ohmic and the SCLC regimes. The resistance R and the excess noise $\mathcal{S}(f)$ observed in a percolative system are described by means of the relationships [25–28]:

$$R = \frac{1}{I^2}\sum_{\alpha} r_\alpha i_\alpha^2 \tag{3}$$

$$\mathcal{S}(f) = s_\Omega(f)\frac{\sum_\alpha i_\alpha^4}{(\sum_\alpha i_\alpha^2)^2}, \tag{4}$$

where i_α is the current flowing through the elementary resistances r_α forming the network. I is the total current, $s_\Omega(f)$ indicates the noise spectral density of the conductive elements of the network. The resistance R and the excess noise $\mathcal{S}(f)$ progressively increase as the conductive matrix becomes sparse according to the relationships:

$$R \propto (\Delta\phi)^{-t} \tag{5}$$

$$\mathcal{S} \propto (\Delta\phi)^{-k} \tag{6}$$

where ϕ represents the conductive volume fraction, while t and k are critical exponents depending on the structure, composition and conduction mechanism of the percolative system. The t and k values depend on the model (e.g. lattice, random void (RV), inverted random void (IRV)) adopted to describe the system [1,26].

An expression of $\mathcal{S}(f)$ in terms of physical observable depending upon the external drive has been worked out in [6]. During trap-filling, the conductive site fraction of the network is reduced proportionally to the difference between the free and trapped charge carrier densities. It is:

$$\Delta\phi \propto \frac{n - n_t}{N_v} \tag{7}$$

where n and n_t are respectively the free and trapped charge carrier densities, N_v is the total density of states, coinciding with the molecular density for narrow band materials as polyacenes. It is convenient to write equation (7) as:

$$\Delta\phi \propto \frac{n}{N_v}\left(1 - \frac{n_t}{n}\right). \tag{8}$$

By comparing equations (7) with (1), it follows that the noise, exceeding the level that would be expected for an homogeneous conductor with comparable density of free charge, arises from the term $(1 - n_t/n)$, i.e. from the imbalance between free and trapped carriers, causing the departure from the quasiequilibrium ohmic conditions. Assuming for simplicity a discrete trap level, it is $n = N_v \exp[-(E_v - E_F)/kT]$ and $n_t = N_t/\{1 + g^{-1}\exp[-(E_F - E_t)/kT]\} \simeq 2N_t \exp[(E_F - E_t)/kT]$, E_F being the quasi-Fermi level, g the degeneracy factor of the trap, N_t is the total density of deep traps and the other quantities have the usual meaning [14]. The resistance R and the excess noise $\mathcal{S}$ diverge at the percolation threshold ϕ_c according to the relationships: $R \propto (\phi - \phi_c)^{-t}$ and $\mathcal{S} \propto (\phi - \phi_c)^{-k}$. The percolation threshold ϕ_c and the onset of breakdown were obtained

as a consequence of additional traps progressively formed by bias or thermal stress, that through the increase of the trap density N_t, enhance the unbalance between free and trapped charge carriers n_t/n [6].

The organic material has been figured as a binary phase system where the transport is confined to narrower and narrower conductive paths worn away by larger and larger insulating regions as the voltage increases. In the remainder of the paper we will add further insights into the percolative fluctuation model by arguing on the relationships between thermal and injected charge carrier densities. These relationships will be then used to show that the observed behavior could not have been deduced as linear superposition of the fluctuations of the two diverse components, therefore evidencing of the percolative mechanism of the fluctuations. In summary, this study demonstrates that an investigation accounting for the statistical properties, namely the charge carrier fluctuations, might be a key to unravel many puzzling phenomena related to the physics of organic and polymeric materials. Pure organic materials could be considered *perfect insulators*, i.e. materials that, under an applied voltage, carry a negligible current associated to the injection of charges according to a mechanism, similar to the emission from a thermionic cathode into vacuum, known as SCLC, analytically described by the *Child law*. Compared to vacuum, the description of the space-charge-limited current in organic and inorganic solids requires to keep into account the complications arising from the electron-phonon interactions. Additional issues arise if chemical impurities and structural imperfections are to be taken into consideration as it always happens in real as opposed to ideal organic insulators. As a matter of fact, the onset of charge injection under SCLC conditions from the electrode critically depends on the presence of deep and shallow energy states related to the unavoidable defects at the metal-organic interface and in the bulk. The curve in Figure 1 exemplifies the typical behavior of the steady-state SCLC in materials with deep traps. The low-voltage region, with slope $l \approx 1$, corresponds to the *ohmic* regime with a current density described by:

$$J_\Omega = \frac{e\mu n V}{L}. \tag{9}$$

The high-voltage region, with slope $l \approx 2$, corresponds to the trap-free space-charge-limited-current regime, obeying the *Mott-Gurney law*:

$$J_{\rm SCLC} = \frac{9\epsilon\epsilon_0\mu\Theta V^2}{8L^3} \tag{10}$$

where Θ is the trapping parameter and the other quantities have the usual meaning. The current-voltage characteristic in the intermediate voltage region, the trap-filling transition (TFT), is analytically described by the *Mark-Helfrich law* [14]:

$$J_{\rm TFT} = N_v\mu e^{1-l}\left[\frac{\epsilon l}{N_t(l+1)}\right]^l \left(\frac{2l+1}{l+1}\right)^{(l+1)} \frac{V^{l+1}}{L^{2l+1}}. \tag{11}$$

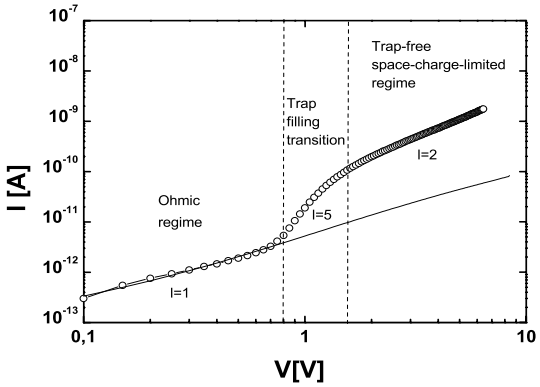

Fig. 1. Log-log plot of the $I-V$ characteristics for a tetracene sample Au/Tc/Al with $L = 0.65$ μm (circles) exhibiting the typical behavior of steady-state SCLC in materials with deep traps (ohmic regime⇒trap-filling transition⇒SCLC regime). The solid line corresponds to the fully ohmic behavior over the entire voltage range.

The current crossing the material under SCLC regime is carried by the injected carriers n_{inj}, depending on V according to:

$$n_{inj} = \frac{\epsilon\epsilon_0}{eL^2}\, V. \tag{12}$$

The ohmic regime described by equation (9) dominates up to a voltage, the threshold voltage V_t, where the injected free charge carrier density becomes comparable to the thermal concentration. Furthermore, one can assume that the injected charges have completely filled the traps at V_t, as expressed by the relationship:

$$n_{inj}(V_t) \approx n_t(V_t). \tag{13}$$

At the crossover from ohmic to SCLC regime, the charge carrier transit time $\tau_t = L^2/\mu V$ and the dielectric relaxation time $\tau_r = \epsilon\epsilon_0/en\mu$ become comparable, i.e. $\tau_t = \tau_r$. This further condition provides a relationship for the threshold voltage $V_t = N_t eL^2/\epsilon\epsilon_0$.

The sudden increase exhibited by the current at the trap-filling transition is customarily estimated by assuming that it takes place over a voltage range $\delta V_t = V_{tf} - V_t$ which is proportional to the threshold voltage V_t, i.e $\delta V_t = cV_t$ and $V_{tf} = (c+1)V_t$ (for the curve shown in Fig. 1 it is $V_t \simeq 0.8V$, $V_{tf} \simeq 1.6V$, $c \simeq 1$). Therefore, because of the proportionality between the injected charges and the voltage [Eq. (12)], the change of injected charges over δV_t is given by:

$$\delta n_{inj} = n_{inj}(V_{tf}) - n_{inj}(V_t) = (c-1)n_{inj}(V_t). \tag{14}$$

Since, on the average, the traps are completely filled at V_t, the additional charge n_{inj} must all appear in the valence band (respectively in the conduction band for electron conduction). The trap filling process is thus accompanied by a conductivity change $\delta\sigma = e\mu\delta n_{inj}$, given by:

$$\delta\sigma = \frac{\partial\sigma}{\partial V_t}\delta V_t = e\mu(c-1)n_{inj}(V_t), \tag{15}$$

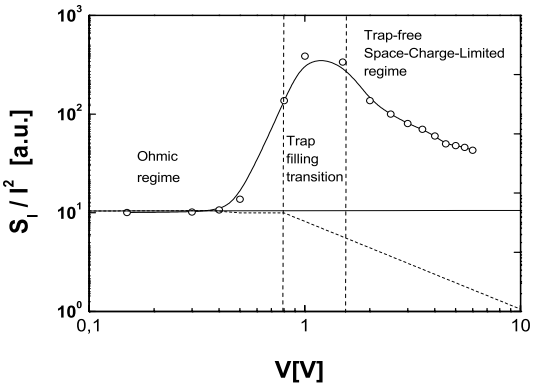

Fig. 2. Log-log plot of the voltage dependence of the relative fluctuation power spectral density at frequency $f = 20$ Hz for the Au/Tc/Al sample (circles). The horizontal solid line, given for reference purpose, corresponds to the behavior expected for ohmic transport over all the voltage range. The dot line, given for reference purpose, represents the decreasing behavior that would be observed in an homogeneous system undergoing a crossover from ohmic to SCLC conduction.

that accounts for the current increase. The latter relationship could be obtained also by using the *regional approximation* approach [14], that is however beyond the scope of the present discussion.

The relationships (12)–(15) will be now used to argue on the need of the percolation picture for the current fluctuations observed at the trap-filling transition. If the transport process would occur in an homogeneous system, with unchanged volumes of the conductive and insulating phase, the relative noise $\mathcal{S}(f)$ could have been evaluated using equation (1). The increase of n, due to the contribution of the injected n_{inj} charge carriers, would thus result in a decrease of the relative noise. The hypothetical behavior that would be obtained for the homogeneous conductor is represented by the dot line in Figure 2. This behavior is of course opposed to the noise increase experimentally observed. The charge carrier trapping results in the formation of insulating regions and forces the current to flow across narrower and narrower conductive paths. The dynamic evolution of such a complex structure, where the charge carrier transport takes place, is clearly deduced from the occurrence of a relative noise peak. It could not have been a priori deduced from the $I-V$ characteristics, that, as we have argued above, will lead to the opposite result. The high sensitivity of the noise to the dynamic of the underlying conductive patterns is well-known: the current noise is proportional to the fourth moment while the conductance is proportional only to the second moment of the current distribution. The behavior exhibited by the organic system is analogous to other complex systems that spontaneously tend to form patterns with varying size and scale over time (self-organization). In such systems, the emergence of an aspect (e.g. giant magnetoresistance, high-T_c superconductivity, metal-insulator transition) could not be derived as a linear superposition of the properties of the single constituents.

Let us finally discuss the extent validity of the percolation fluctuation model [1,27,28] with particular regards to the organic materials. As already stated, the relationships (3)–(6) apply only to ohmic and trap-filling regions of the $I-V$ characteristics, i.e. in the subnetwork where transport mostly takes place by continuum metallic conduction. As the trap-free SCLC regime is approached, a condition guaranteed by the onset of the 2-sloped $I-V$ curve, the noise mostly arises from a mechanism different than the charge carriers density and/or mobility fluctuations. The current is governed by the process of injection and thus the noise is very likely originated by fluctuations of the probability of emission or tunnelling across a potential barrier. The mechanism is, for certain aspects, analogous to the shot noise, $S_{\rm shot} = 2eI\Gamma$, observed in vacuum tubes or solid state junctions, where the space charge, built-up in the interelectrode region, acts with a negative feedback effect on the fluctuations [6]. Such a noise mechanism could indeed explain the decrease of the relative fluctuations observed when the trap-free space-charge-limited conduction is fully achieved. A more complicated relationship than $S_{\rm shot} = 2eI\Gamma$ should be however expected, due to the correlated hopping events and polaronic effects in organic semiconductors. Another limit is represented by the fact that the percolation process through a two-component disordered system, made of ohmic and SCLC elements, is not exactly described by equations (3)–(6). In fact, these expressions contemplate the case of a metal-insulator mixture with the insulator carrying no current at all [27]. The two-components percolative theory is not adequate to the description of the present case, as well. In fact, a matrix formed by two components having different ohmic conductivities, with the current fluctuations arising from the same mechanism is dealt with in [28]. The analytical treatment of the percolative fluctuations in a disordered space-charge-limited conductor would require that two different mechanisms of noise related respectively to the ohmic and to the SCLC phases, are taken into account.

To conclude, the investigation of current noise in polycrystalline polyacenes has revealed: (i) a *steady-state ohmic fluctuation regime* at low-voltage; (ii) a *critical fluctuation regime*, at the trap filling transition, interpreted within a continuum percolation model; (iii) a *steady-state space-charge-limited-current fluctuation* regime at high voltage. The current noise depends on the topological disorder due to inhomogeneously distributed traps in the layer and thus it can provide clues in a microscopic description of transport in organic materials. These systems are characterized by distributed thresholds for conduction, due to local inhomogeneous traps and barriers of varying strength. The dynamical processes by which such systems undergo a transition from order to disorder driven by an external bias, are issues of general interest well beyond the field of organic electronics. The cooperative effect of charge, spin, lattice or impurity interactions, that could not be predicted on the basis of the *average* superposition of the elementary constituents, is at the origin of the giant fluctuations in such systems. The relevant implication is that the observed behavior has to be considered as an

emergent phenomenon, within the broader context of the electronic complexity.

Future issues to be investigated include experiments to observe *space-charge-limited current fluctuations* in diverse materials and operative conditions. The development of a theoretical model of the percolative fluctuations, including two different noise components, will also represent an advancement in this field.

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