Unified Mobility Model for Amorphous Organic Materials

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***Abstract*—The influence of temperature, carrier concentration and electric field on the hopping transport in disordered organic semiconductors is studied theoretically, and a simple and accurate analytical model is worked out. The model is based on the concept of percolation in a variable range hopping system and the calculations are worked out exploiting the effective temperature approach. At room temperature the dependence on carrier density plays a major role, whereas at low temperatures or high fields the electric field dependence becomes relevant. Neglecting only one of those effects, depending on the operating conditions, leads to an evident underestimation of the hopping mobility.**

***Index Terms*—VRH transport, percolation theory, DOS**

I. INTRODUCTION

The interest in organic electronic stems from the the ability to deposit organic films on a variety of low-cost substrate such as glass, plastic or metal foils, and the relative easy of processing of the organic compounds. The use of amorphous organic semiconductors in light emitting devices (OLEDs) and field-effect transistors (OFETs) has triggered an intensive research on their optoelectronic and electrical transport proprieties [1]. Understand the charge transport is of crucial importance to design and synthesize better materials and to improve device performance. One of the most important parameters that determine the devices performances is the carrier mobility μ. In particular, the dependence of μ on temperature T and electric field F and carrier density has been extensively addressed in the literature [2], [3], [4], and several models that separately account for each of them were proposed [5], [6]. On the other hand, a clear physical picture of the mobility that globally accounts for the relative effects of temperature, carrier density, and electric field, is still absent in the literature. Experimentally, it is difficult to separate the relative importance of electric field and carrier density on the mobility μ since, at high electric fields, the carriers are more efficiently injected from the contacts as well. In Ref. [7] the carriers dependence of μ was explained by means of an empirical expression based on the algebraic expression of Vissenberg and Matters $\mu \propto p^{T_0/T-1}$ [8] slightly modified by adding a density-independent contribution empirically introduced from the current-voltage characteristics of hole-only diodes. That empirical expression does not correctly account for the experimental current-voltage characteristics at low temperatures and at high voltages; it was attributed to an unknown dependence of μ on the electric field.

Aim of this work is to derive a mobility model that accounts, in a single analytical expression, for the most relevant physical quantities: temperature T, carrier concentration δN_t, and electric field F. The model is based on the concept of percolation in a Variable Range Hopping system (VRH) with an exponential distribution of localized-energy states (DOS) [8] and the mathematical calculations are worked out by exploiting the well accomplished effective temperature approach [9], [10], [11], [12]. It accurately reproduce experiments and numerical simulations and provides, by means of a single mathematical expression, a clear picture of several physical effects as, for instance, the Poole-Frenkel like dependence of the mobility on the electric field or the Arrhenius dependence on temperature. We expect that this mobility theory enables predictive models for disordered organic devices based on parameters that may be determined *ab initio* from measurements. Furthermore, thanks to its simple analytical formulation, the relative importance of temperature, carrier density, and electric field could singularly investigated and disentangled on the experimental results.

II. THEORY: MODEL DERIVATION

Charge transport in disordered organic semiconductors is governed by hopping through localized states. The conductance between two sites is proportional to the occupation probability of the site that release the carrier, called donor, the occupation probability of the site that receive the carrier, called acceptor, and the hopping rate between the two sites:

$$G_{ij} = G_0 f(E_i, E_F)\left[1 - f(E_j, E_F)\right]\nu_{ij} \tag{1}$$

where G_0 is a constant prefactor and E_F is the Fermi energy level. In presence of an electric field $\mathbf{F}$ the Miller-Abrahams hopping rate [13], from a donor at energy E_i to an acceptor at energy E_j at a distance r_{ij}, can be re-written as:

$$\nu_{ij} = \nu_0 \exp\left[-2\alpha r_{ij}\right] \exp\left[\frac{-||E_j - E_i - \mathbf{F}\cdot\mathbf{r}_{ij}||}{2K_B T}\right] \tag{2}$$

where ν_0 the attempt-to-escape frequency, α^{-1} the localization radius of a charge carrier, $\mathbf{r}_{ij}$ the distance between the two sites, K_B the Boltzmann constant, T is the temperature and $||x|| = x + |x|$.

Furthermore, the occupation probability should be worked out in order to include the local variation of E_F arising from the external electric field, and the Fermi-Dirac distribution

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should be generalized to non-equilibrium. The non-equilibrium occupation probability is accurately accounted for by replacing the lattice temperature T in the Fermi-Dirac statistic with an effective temperature T_{eff} that, in turn, is a function of the electric field [12]:

$$f(E,E_F)=\frac{1}{1+\exp\left[\frac{E-E_F}{K_B T_{eff}}\right]} \tag{3}$$

and

$$T_{eff}=\left[T^{\beta}+\left(\gamma\frac{eF}{\alpha K_B}\right)^{\beta}\right]^{1/\beta} \tag{4}$$

where β and γ are fitting parameters ($\beta=2$, $\gamma=0.67$ [10]; $\beta=1.54$, $\gamma=0.64$ [12]) and e is the elementary charge.

By assuming $E>E_F+2K_BT_{eff}$ and $E_j>E_F+2K_BT$, that is K_BT_{eff}, small compared to all the energy of the system, the non-equilibrium occupation probability can approximated by the Boltzmann distribution and the non-equilibrium conductance between the sites can be re-written in a very simple form:

$$G_{ij}=G_0\exp[-s_{ij}] \tag{5}$$

where s_{ij} is:

$$s_{ij}=2\alpha r_{ij}+\begin{cases}\frac{\frac{T_{eff}}{T}E_j^{'}-E_F+\frac{T-T_{eff}}{T}E_i}{K_BT_{eff}}, & E_j^{'}>E_i\\ \frac{E_i-E_F}{K_BT_{eff}}, \quad E_j^{'}\leq E_i\end{cases} \tag{6}$$

and $E_j^{'}=E_j-e\eta Fr_{ij}$, $\eta=\eta(\theta,\varphi)=sin(\theta)sin(\varphi)$. It is worth noting, that the largest percentage error introduced by the above approximation, with respect to the exact solution, is about 12% in a small energy region around to the Fermi level (where $|E-E_F|<K_BT_{eff}$). In other words, the probability to find an empty site is assumed equal to one, and the conductance between two site dependes only on the hopping rate and on the probability to find an occupied donor site.

According to the percolation theory [8], [14], the system is treated as a random resistor network that connects the molecular sites. To determine the conductivity of the disordered system, we take a reference conductance G and remove all the conductive pathways between sites with $G_{ij}<G$. At large G, the remaining conductances form isolated clusters that increase in size with decreasing G. The critical percolation conductance $G_c=G_0\exp[-s_c]$ is defined as the value of G such that the first continuous infinite cluster is formed. According to the percolation theory [14], the conductivity of the system reads:

$$\sigma=\sigma_0\exp[-s_c] \tag{7}$$

where σ_0 is an constant prefactor and s_c is the exponent of the critical percolation conductance G_c at which this percolation threshold is reached. The onset of percolation is determined by calculating the average number of bonds ($G_{ij}>G$) per site in the largest cluster, this number of bonds B increases with decreasing G as far as, at the onset of percolation, the critical number of bonds B_c is reached. The onset of percolation is determined by calculating the critical average number of bonds per site:

$$B\left(G=G_c\right)=B_c=\frac{N_b(s_c,E_F)}{N_s(s_c,E_F)} \tag{8}$$

where $B_c=2.8$ for a 3-D amorphous system [15], N_b and N_s are the density of bonds and the density of sites in a percolation system, respectively. The total density of bonds can be calculated by integrating in energy, over the distance r_{ij}, the product of all donor sites (at energy E_i) and all the available acceptor states (at energy E_j) that satisfy the percolation criterion:

$$\begin{aligned}N_b &= \int_{\mathbb{R}^5} g(E_i)g(E_j)\theta\left(s_c-s_{ij}\right)dE_jdE_idx_{ij}dy_{ij}dz_{ij}\\ &= \int_0^{2\pi}\int_0^{\pi}\sin\left(\theta\right)\int_0^{\frac{sc}{2\alpha}}r_{ij}^2\int_{E_F}^{E_F+U_F^i}g\left(E_i\right)\times\\ &\quad\times\int_{E_F}^{\frac{T}{T_{eff}}\left(E_F+U_F^j\right)}g\left(E_j\right)dE_jdE_idr_{ij}d\theta d\varphi\end{aligned} \tag{9}$$

where $r_{ij}=\sqrt{x_{ij}^2+y_{ij}^2+z_{ij}^2}$, $g(E)$ is the density of localized states and U_F^k, $k=\{i,j\}$ is the maximum hopping energy that, from Eq. 6, turns out to be:

$$U_F^i = K_BT_{eff}\left(s_c-2\alpha r_{ij}\right) \tag{10}$$

$$U_F^j = U_F^i-\left(\frac{T-T_{eff}}{T}\right)E_i+e\frac{T_{eff}}{T}\eta Fr_{ij} \tag{11}$$

The density of sites N_s that satisfy the percolation criterion is:

$$N_s=\int_{E_F}^{E_F+U}g(E)\;dE \tag{12}$$

where $U=U_F^i\left(r_{ij}=0,F=0\right)=K_BTs_c$. Following Vissenberg and Matters [8], at low carrier densities, the transport properties are determined by the tail of the density of the localized states $g(E)=\frac{N_t}{k_BT_0}\exp\left(\frac{E}{k_BT_0}\right)$, where N_t is the number of states per unit volume, T_0 is a parameter related to the system disorder, and $g(E)=0$ for positive values of E. Since an occupied donor site, after a carrier hopping, becomes an empty acceptor site, it is conventionally assumed that donor and acceptor sites have the same DOS. The exact conductivity σ_{NE} of an amorphous organic material can be calculated by replacing in Eq. 7 the critical percolation conductance exponent s_c numerically calculated from Eq. 8.

The influence of the electric field on the hopping between sites is accounted for by means of an energy shift due to the potential energy (Eq. 2) arising from the electric field, along with a redefinition of the carriers occupation probability (Eq. 3) that should be generalized to non equilibrium Eq. 4. Since the energy shift depends on the hopping direction and the maximum hopping distance, we expect it to weakly influence the overall system conductivity. In order to evaluate its relative importance on the overall conductivity, Eq. 8 has been solved neglecting the electric field contribution in Eq. 11 and the conductivity σ_{NA} has been obtained. In Fig. 1 the

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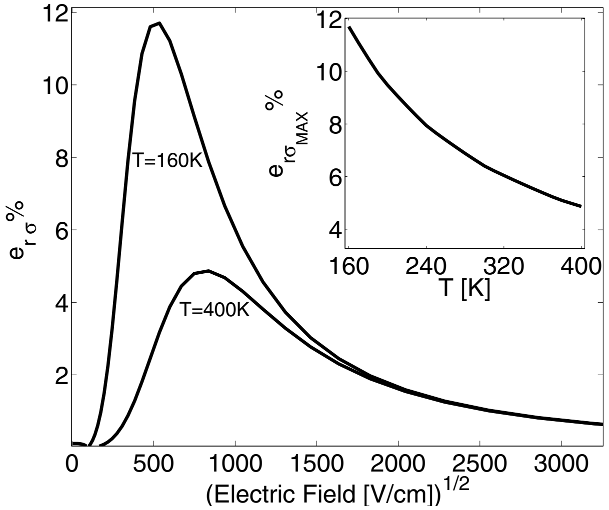

Fig. 1. Relative conductivity error ($e_{r_\sigma}\% = 100\left|\sigma_{NE} - \sigma_{NA}\right|/\sigma_{NE}$) as a function of electric field at different temperatures. Inset: maximum relative conductivity error as a function of temperature T.

relative conductivity error ($e_{r_\sigma} = \left|\sigma_{NE} - \sigma_{NA}\right|/\sigma_{NE}$) as a function of electric field at different temperatures is reported. The largest error is below 12% and decrease with temperature (from about 12% at T=160K to 5% at T=400K). Therefore, in order to work out a full analytical expression, its contribution can be neglected and Eq. 11 can be simplified as:

$$U_F^j = U_F^i - \left(\frac{T - T_{eff}}{T}\right) E_i \qquad (13)$$

and Eq. 9 does not depend on θ and φ. Furthermore, thanks to the proprieties of the exponential function $g(E)$, when the hopping energy U is larger then few thermal units ($U \geq 3K_BT_0$), the lower extreme of the integrals (Eqs. 9, 12) is vanishing and the polygonal integration domain can be simplified by a semi-infinite region and Eqs. 9, 12 can be simplified as:

$$\begin{aligned} N_b &= 4\pi \int_0^{\frac{sc}{2\alpha}} r_{ij}^2 \int_{-\infty}^{E_F+U_F^i} g\left(E_i\right) \times \\ & \int_{-\infty}^{\frac{T}{T_{eff}}\left(E_F+U_F^j\right)} g\left(E_j\right) dE_j dE_i dr_{ij} \end{aligned} \qquad (14)$$

where U_F^j is given by Eq. 13 and

$$N_s = \int_{-\infty}^{E_F+U} g(E)\ dE \qquad (15)$$

Substituting Eqs. 14, 15 into Eq. 8 the percolation criterion is obtained:

$$B_c \approx \frac{\pi N_t T_0^3}{\left(2\alpha\right)^3 T_{eff}^2 \left(2T_{eff} - T\right)} \exp\left[\frac{E_F + K_B T_{eff} s_c}{K_B T_0}\right] \qquad (16)$$

where it is assumed that the maximum energy hop is large ($s_cK_BT >> K_BT_0$) [8], and that the hopping takes place between localized states. Combining Eq. 7 and 16, the expression of the conductivity as a function of electric field, Fermi level and temperature reads:

$$\sigma = \sigma_0 \left[\frac{\pi N_t T_0^3}{\left(2\alpha\right)^3 B_c T_{eff}^2 \left(2T_{eff} - T\right)}\right]^{\frac{T_{eff}}{T_0}} \exp\left[\frac{E_F}{K_B T_{eff}}\right] \qquad (17)$$

The Fermi level can expressed as a function of the carrier concentration since:

$$\begin{aligned} \delta N_t &= \int_{-\infty}^{+\infty} g(E) f(E, E_F) dE \\ &\approx N_t \left(\frac{\pi T/T_0}{sin(\pi T/T_0)}\right) \exp\left[\frac{E_F}{K_B T_0}\right] \end{aligned} \qquad (18)$$

where δN_t is the fraction of localized states occupied by carriers, $\delta \in [0, 1]$ (δN_t is the electron/hole concentration depending on the device type). In Eq. 18 it is assumed a high level of disorder ($T_0 > T$), hence only the tail of the DOS is relevant since the carriers are located far from $E = 0$. Combining Eqs. 17, 18 the analitic expression of the mobility of disordered organic material as a function T, δN_t, and F is:

$$\mu = \frac{\sigma_0}{e} \left[\frac{T_0^4 sin\left(\pi \frac{T}{T_0}\right)}{B_c \left(2\alpha\right)^3 T_{eff}^2 \left(2T_{eff} - T\right) T}\right]^{\frac{T_0}{T_{eff}}} \left(\delta N_t\right)^{\frac{T_0}{T_{eff}} - 1} \qquad (19)$$

It is worth noting that if $F \rightarrow 0$, $T_{eff} \rightarrow T$ the above equation is exactly the same of [8].

III. MODEL VALIDATION

In order to investigate the accuracy of our model when $F > 0$, it is compared with the numerical solution of the master equation of [12] that has been proved to accurately reproduce the current-voltage characteristics of both light emitting diodes and field effect transistors. In Fig. 3, the mobility as a function of the temperature at different electric fields is compared with [16] as well.

The parameters of our model ($N_t = 10^{21} cm^{-3}$, $T_0 = 470K$, $\sigma_0 = 3\nu_0\ 10^{-19} S/cm$, $\alpha^{-1} = 1.8\mathring{A}$, $\gamma = 0.7$, $\beta = 1.72$) are in a very good agreement with the literature: N_t and α are the same of [16], T_0 is straightforwardly derived following [17], γ and β are fitting parameters [12]. The two models are in perfect agreement, and when $F > 3 \times 10^5 V/cm$ the well known Pool-Frenkel behavior $\mu \propto \exp[\gamma\sqrt{F}]$ is correctly reproduced. Hence, as reported in [16] there is no need to assume spatial energy correlation, as suggested by several authors, and the sites may be assumed uncorrelated. As reported in [7], [17] the mobility is strictly correlated to the carrier density that, in turn, depends on the shape of the density of states; it follows that our model correctly approximate the numerical solution of [16], that is based on a gaussian DOS, only locally. Therefore, the characteristic parameters of the exponential distribution, N_t, T_0 should be slightly modified when the mobility is calculated at large carrier concentrations (FET devices) or at low carriers concentrations (LED devices) [17]. In Fig. 3, the mobility as a function of the temperature is compared with [16] as well. The two models are in perfect agreement and the mobility, as reported in [18] is clearly

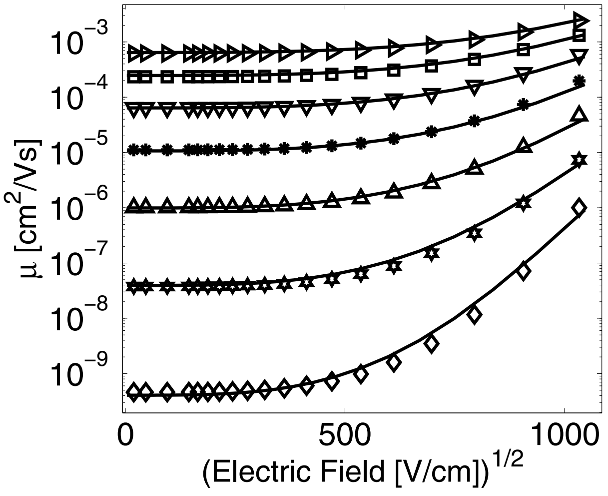

Fig. 2. Numerical (symbols) and analytical (lines) mobility as a function of the electric field at different temperatures for NRS-PPV.◇ T=160K, ⋆ T=200K, △ T=240K, ∗ T=280K, ▽ T=320K,□ T=360K, ▷ T=400K.

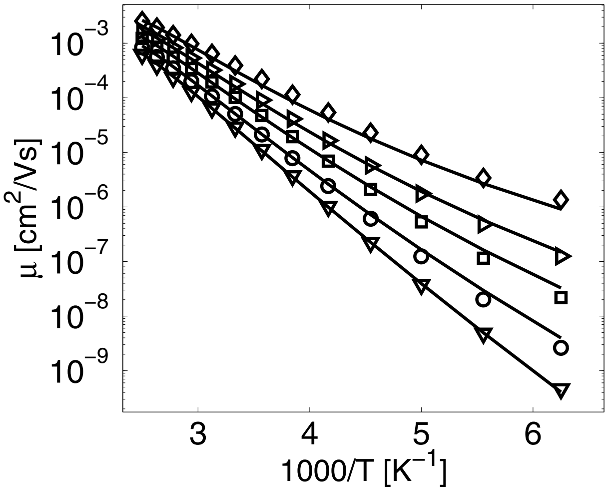

Fig. 3. Numerical (symbols) and analytical (lines) mobility as a function of the temperature at different electric fields for NRS-PPV. ▽ F=0 V/cm, ○ F=0.5 MV/cm, □ F=0.7 MV/cm, ▷ F=0.88 MV/cm, ◇ F=1.1 MV/cm.

consistent with an Arrhenius temperature dependent transport.

IV. CONCLUSION

To conclude, in this paper we have presented an unified description of the carrier mobility in disordered organic materials. The model is based on the concept of percolation in a variable range hopping system and the effect of the electric field is accounted for by exploiting the effective temperature approach. The calculations are carried out by critically investigating the approximation introduced by the above authors and are worked out following a new straightforward mathematical approach. It accurately reproduce experiments and numerical simulations and provides, by means of a single mathematical expression, a clear picture of several physical effects as the Poole-Frenkel like dependence of the mobility on the electric field or the Arrhenius behavior on temperature.

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