

# Analytical conductivity model for doped organic semiconductors

Ling Li,<sup>a)</sup> Gregor Meller, and Hans Kosina*Institute for Microelectronics, TU Vienna, Gußhausstraße 27–29, A–1040 Wien, Austria*

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Charge transport in doped organic semiconductors is investigated, and an analytical conductivity model is proposed based on the variable range hopping theory. The model can well explain the superlinear increase of the conductivity with doping, as well as the change in the conductivity of an organic semiconductor upon the doping ratio. The model demonstrates that the exponent of an empirical power law for the conductivity is actually temperature-dependent. Calculation results coincide well with experimental observations. © 2007 American Institute of Physics.

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## I. INTRODUCTION

Ever since the discovery of electroluminescence in the conjugated polymer PPV<sup>1–14</sup> and its derivatives, there has been growing interest in the study of the (opto)electronic and electrical transport properties. A thorough understanding of these properties will be of crucial importance to the design and synthesis of better organic materials, with the hope to improve the performance of a wide range of organic devices.

In organic semiconductors, intramolecular interactions are mainly covalent, while intermolecular interactions are usually induced by the much weaker van der Waals and London forces. As a result, the transport bands in organic crystals are much narrower than those of their inorganic counterparts, and the band structure is easily broken by disorders in such systems, leading to localized states in the energy gap. A well-known theory by Conwell<sup>2</sup> and Mott<sup>8</sup> assume that the conduction process in organic materials is entirely determined by the tunneling transitions of carriers between these localized states, provided that the electronic wave functions of the localized states have sufficient overlap. This was later studied more systematically by Mott,<sup>14</sup> who proposed the variable range hopping (VRH) theory. The transport properties of many organic semiconductors can be well described by the VRH theory.<sup>11,15–18</sup>

Despite decades of researching progress, however, some rather ubiquitous features of the charge transport in organic semiconductors are still far from being well understood. One such example is the relation between conductivity and doping.<sup>19–21</sup> Although the doping process of organic semiconductors can largely be depicted by a standard model used for crystalline inorganic semiconductors,<sup>5</sup> a general doping model still remains a challenge for organic semiconductors. For instance, it is not clear whether the dopants are homogeneously distributed in the material. In particular, for some experiments<sup>18</sup> a strong superlinear increase of the conductivity with doping is observed.

In this work, we present an analytical model for hopping transport in doped, disordered organic semiconductors based on the VRH and the percolation theory. This model can suc-

cessfully explain the superlinear increase of conductivity with doping observed in several experimental data sets.

## II. MODEL THEORY

For a disordered organic semiconductor system, we assume that localized states are randomly distributed in both the energy and the coordinate space, and that they form a discrete array of sites. Conduction proceeds via hopping between these sites. In the case of low electric field, the conductivity between site  $i$  and site  $j$  can be calculated as<sup>10</sup>

$$\sigma_{ij} \approx \gamma \exp\left(-2\alpha R_{ij} - \frac{|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_i - \varepsilon_j|}{2k_B T}\right), \quad (1)$$

where  $\varepsilon_i$  and  $\varepsilon_j$  are the energies at the sites  $i$  and  $j$ , respectively,  $\varepsilon_F$  is the Fermi-energy,  $R_{ij}$  is the distance between sites  $i$  and  $j$ , and  $\alpha^{-1}$  is the Bohr radius of the localized wave function. The first term  $2\alpha R_{ij}$  is a tunneling term, and the second one is a thermal activation term (Boltzmann term).

For organic semiconductors, the manifolds of both the lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO) are characterized by random positional and energetic disorder. Being embedded into a random medium, similarly, dopant atoms and molecules are inevitably subjected to the positional and energetic disorder, too. Since the HOMO level in most organic semiconductors is deep and the gap separating LUMO and HOMO states is wide, energies of donor and acceptor molecules are normally well below LUMO and above HOMO. Therefore, we assume a double exponential density of states

$$g(\varepsilon) = \frac{N_i}{k_B T_0} \exp\left(\frac{\varepsilon}{k_B T_0}\right) + \frac{N_d}{k_B T_1} \exp\left(\frac{\varepsilon - E_d}{k_B T_1}\right) \quad (\varepsilon \leq 0), \quad (2)$$

where  $N_i$  and  $N_d$  are the concentrations of the intrinsic and the dopant states, respectively,  $T_0$  and  $T_1$  are parameters indicating the width of the intrinsic and the dopant distributions, respectively, and  $E_d$  is the Coulomb trap energy.<sup>13</sup> Visserberg and Matters pointed out that they do not expect the results to be qualitatively different for a different choice of  $g(\varepsilon)$ , as long as  $g(\varepsilon)$  increases strongly with  $\varepsilon$ . Therefore, we

<sup>a)</sup>Electronic mail: li@iue.tuwien.ac.at

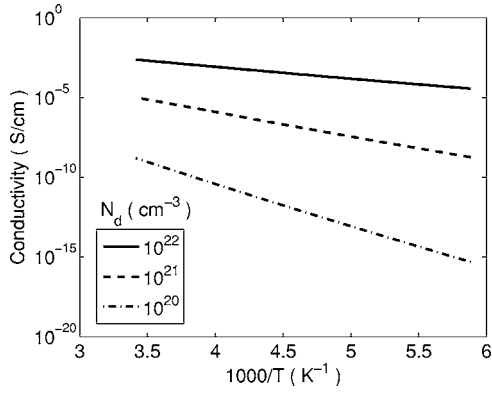


FIG. 1. Temperature dependence of the conductivity in a disordered hopping system at different doping concentrations.

assume that transport takes place in the tail of the exponential distribution.

The equilibrium distribution of carriers,  $\rho(\varepsilon)$ , is determined by the Fermi-Dirac distribution  $f(\varepsilon)$  as follows:

$$\rho(\varepsilon) = g(\varepsilon)f(\varepsilon) = \frac{g(\varepsilon)}{1 + \exp[(\varepsilon - \varepsilon_F)/k_B T]}.$$

The Fermi-energy of this system is fixed by the equation for the carrier concentration  $n$

$$n = \int \frac{d\varepsilon g(\varepsilon)}{1 + \exp[(\varepsilon - \varepsilon_F)/k_B T]} = n_i + n_d, \quad (3)$$

where

$$n_i = N_t \exp\left(\frac{\varepsilon_F}{K_B T_0}\right) \Gamma(1 - T/T_0) \Gamma(1 + T/T_0),$$

$$n_d = N_d \exp\left(\frac{\varepsilon_F - E_d}{K_B T_1}\right) \Gamma(1 - T/T_1) \Gamma(1 + T/T_1).$$

Here,  $\Gamma$  is the gamma function. According to the classical percolation theory,<sup>10</sup> the current will flow through the bonds connecting the sites in a random Miller and Abrahams network.<sup>7</sup> The conductivity of this system is determined when the first infinite cluster occurs. At the onset of percolation, the critical number  $B_c$  can be written as

$$B_c = \frac{N_b}{N_s}, \quad (4)$$

where  $B_c = 2.8$  for a three-dimensional amorphous system,  $N_b$  and  $N_s$  are, respectively, the density of bonds and the density of sites in this percolation system, which can be calculated by<sup>12,22-24</sup>

$$N_b = \int d\mathbf{R}_{ij} d\varepsilon_i d\varepsilon_j g(\varepsilon_i) g(\varepsilon_j) \theta(s_c - s_{ij}), \quad (5)$$

$$N_s = \int d\varepsilon g(\varepsilon) \theta(s_c k_B T - |\varepsilon - \varepsilon_F|). \quad (6)$$

Here  $\mathbf{R}_{ij}$  denotes the distance vector between sites  $i$  and  $j$ ,  $\theta$  is the unit step function, and  $s_c$  is the exponent of the conductance given by the relation<sup>23</sup>

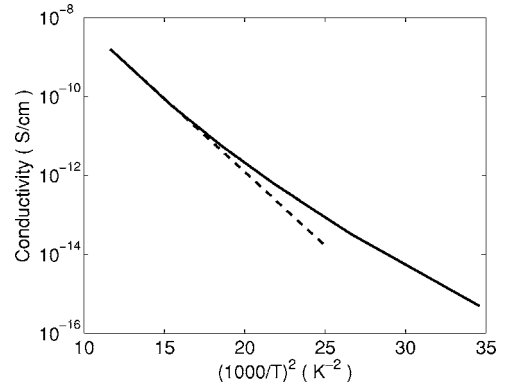


FIG. 2. The temperature dependence of the conductivity in organic semiconductors, plotted as  $\log \sigma$  vs  $T^{-2}$ . The dashed line is to guide the eye.

$$\sigma = \sigma_0 \exp(-s_c). \quad (7)$$

Substituting (2), (5), and (6) into (4), we obtain the expression

$$B_c = \frac{\kappa + p}{N_t \exp(\eta) + N_d \exp(\gamma)}, \quad (8)$$

where

$$\kappa = \pi N_t^2 \psi^3 \exp(2\eta) + \pi N_d^2 \xi^3 \exp(2\gamma),$$

$$p = \frac{\pi}{4} N_t N_d \exp(\eta + \gamma) (\psi^{-1} + \xi^{-1})^{-3},$$

$$\eta = \frac{\varepsilon_F + k_B T s_c}{k_B T_0}, \quad \gamma = \frac{\varepsilon_F - E_d + k_B T s_c}{k_B T_1},$$

$$\psi = \frac{T_0}{4\alpha T}, \quad \xi = \frac{T_1}{4\alpha T}.$$

Equation (8) has been obtained under the following conditions:

- The site positions are random;
- the energy barrier for the critical hop is large compared with  $k_B T$ ;
- and the carrier concentration is very low.

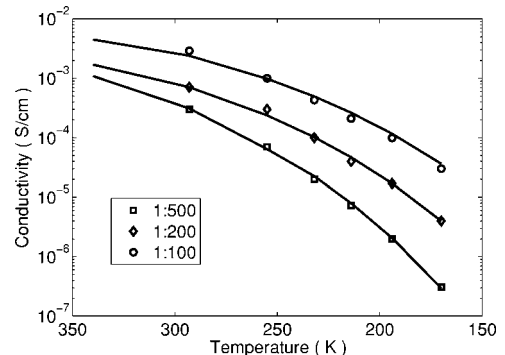


FIG. 3. Conductivity of doped ZnPc at various doping ratios as a function of temperature. The lines represent the analytical model, experiments (symbols) are from Ref. 18.

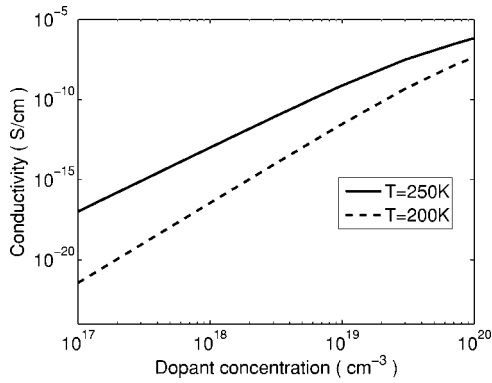


FIG. 4. Conductivity as a function of the dopant concentration with temperature as a parameter.

The exponent  $s_c$  is obtained by a numerical solution of (8) and the conductivity can be calculated using (7).

### III. RESULTS AND DISCUSSION

Figure 1 illustrates the temperature dependence of the carrier conductivity for different doping concentrations. Parameters are  $\alpha^{-1}=0.37 \text{ \AA}$ ,  $E_d=0.5 \text{ eV}$ ,  $T_0=800 \text{ K}$ , and  $T_1=400 \text{ K}$ . The Arrhenius-type temperature dependence

$$\log \sigma \propto -E_A/k_B T,$$

can be observed clearly in Fig. 1. In Fig. 2, we plot the graph  $\log \sigma$  vs  $T^{-2}$ , which is observed to deviate slightly from a straight line (dashed in Fig. 2). This is because, at higher temperatures, almost all the carriers occupy the intrinsic states, therefore the dopants do not change the trap-free hopping relation  $\log \sigma \propto T^{-2}$ .<sup>15</sup> The doping process is quite efficient for ZnPc with dopant F4-TCNQ.<sup>18</sup> In Fig. 3, we compare between the measured conductivity at room temperature and the theoretical curves calculated from (7). The agreement is quite satisfactory. The fit parameters are the same as those used in Fig. 1, and have been chosen according to Ref. 18. From Figs. 1 and 3, we can see that the conductivity increases considerably with the dopant concentration, especially in the lower temperature regime.

The superlinear dependence of conductivity on the doping concentration has been investigated extensively by several groups,<sup>17,19,20</sup> where the empirical formula

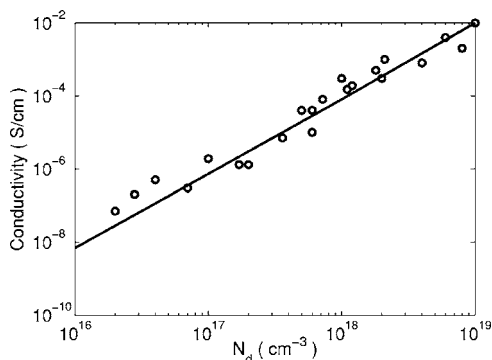


FIG. 5. Conductivity of PPEEB films versus the dopant concentration. The line represents the analytical model. Experiments (symbols) are from Ref. 17.

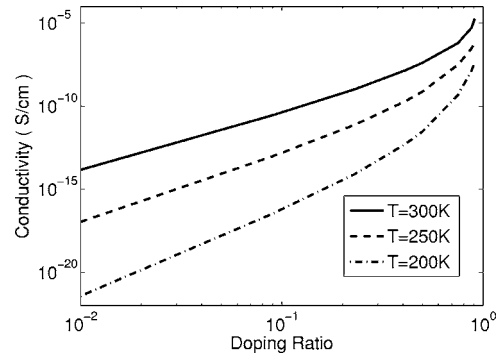


FIG. 6. Conductivity as a function of the doping ratio with temperature as a parameter.

$$\sigma \propto N_d^\gamma,$$

is used to describe this dependence. Using our model, such superlinear increase of the conductivity upon doping can be predicted successfully. We show this in Fig. 4, where the parameters are the same as in Fig. 1. Our model gives  $\gamma=4.9$  for  $T=250 \text{ K}$ , and  $\gamma=3.9$  for  $T=200 \text{ K}$ . Note that these choices are consistent with those in,<sup>19</sup> where the  $\gamma$  is chosen in the range.<sup>3,5</sup> In Fig. 5, we compare the predictions of our model with the experimental data of doped PPEEB.<sup>17</sup> The parameters are  $\alpha^{-1}=6 \text{ \AA}$ ,  $E_d=0.6 \text{ eV}$ ,  $T_0=1000 \text{ K}$ , and  $T_1=500 \text{ K}$ . The predictions fit the experimental data very well.

In Fig. 6, we plot the relation between the conductivity and the doping ratio

$$\frac{N_d}{N_t + N_d},$$

for different temperatures with parameters  $T_0=1000 \text{ K}$ ,  $T_1=500 \text{ K}$ ,  $E_d=0.5 \text{ eV}$ , and  $\sigma_0=1 \times 10^7 \text{ S/cm}$ . We can see that the conductivity increases with both the temperature and the doping ratio. More specifically, there is a transition in the increase of the conductivity of an organic semiconductor upon doping, which is manifested by a change in the slope of the curve as shown in Fig. 7. There we can see that the conductivity increases linearly for low doping levels, and increases superlinearly for high doping levels. This transition has been interpreted in Ref. 13 in terms of the broadening of the transport manifold due to the enhanced disorder from the dopant.

Assuming a simple Arrhenius law

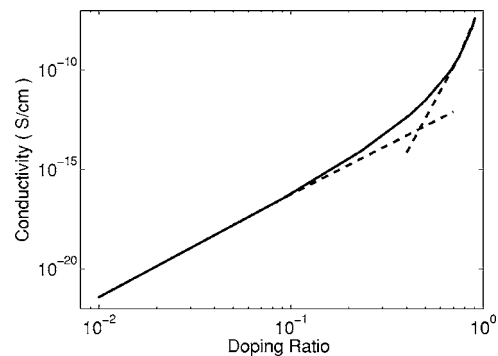


FIG. 7. Conductivity at  $T=200 \text{ K}$  as a function of the doping ratio. The dashed line is to guide the eye.

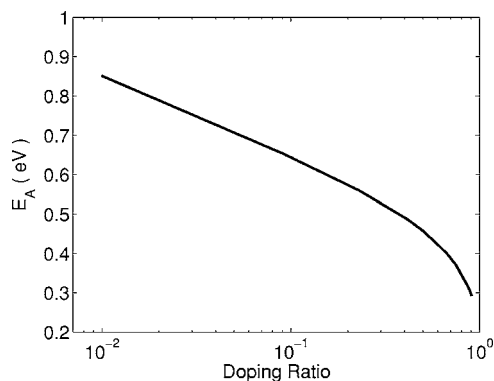


FIG. 8. Activation energy ( $E_A$ ) as a function of the doping ratio.

$$\sigma \propto \exp\left(\frac{-E_A}{k_B T}\right),$$

we can obtain the relation between activation energy  $E_A$  and doping ratio, as shown in Fig. 8. As can be seen,  $E_A$  decreases with the doping ratio, indicating that less and less energy will be required for a carrier activated jump to neighboring sites when the doping ratio increases. Similar to Fig. 7, we can also observe a transition between the two doping regimes visible as a change in the slope.

#### IV. CONCLUSION

We have presented an analytical model to describe the doping-dependent conductivity for organic semiconductors. This model can well explain the Arrhenius-type dependence of conductivity on temperature, i.e., the doping efficiency increases with decreasing temperature. Moreover, a transition in the increase of the conductivity of an organic semiconductor upon the doping ratio, as observed in experimental data, is also successfully described through the model. Comparison with experimental data show that the model is accurate in predicting the relation between the conductivity and the dopant concentration.

#### ACKNOWLEDGMENTS

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