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Theory of the field-effect mobility in amorphous organic transistors

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The field-effect mobility in an organic thin-film transistor is studied theoretically. From a percolation model of hopping between localized states and a transistor model an analytic expression for the field-effect mobility is obtained. The theory is applied to describe the experiments by Brown *et al.* [Synth. Met. **88**, 37 (1997)] on solution-processed amorphous organic transistors, made from a polymer (polythienylene vinylene) and from a small molecule (pentacene). Good agreement is obtained, with respect to both the gate voltage and the temperature dependence of the mobility. [S0163-1829(98)01320-4]

Over the last decade the use of organic p-type semiconductors in field-effect transistors has gained considerable interest due to their potential application in low-cost integrated circuits. Most effort has been put into increasing the hole mobility of the semiconductor and increasing the on-off ratio of the field-effect transistor by optimizing existing materials and by applying new materials. Mobilities as high as 0.7 $cm^2\ V^{-1}\ s^{-1}$ and on-off ratios of 10^8 have recently been reported in thin-film transistors of evaporated pentacene.[1] Furthermore, attention has been focused on the improvement of the processability of these materials by using directly soluble[2] or precursor organic semiconductors.[3] Besides the technical applicability of organic semiconductors, their electronic and structural properties have been the subject of investigation as well. Interesting questions like the connection between molecular order and hole mobility in conjugated oligomers and polymers have been addressed.[1,4–6]

Experiments have indicated that the field-effect mobility of holes in organic transistors depends on the temperature as well as on the applied gate bias.[3,7] This has been described by Horowitz *et al.* using a multiple trapping and release model.[7] In this model the assumption is made that most of the charge carriers are trapped in localized states. Then the amount of (temporarily) released charge carriers to an extended-state transport level (the valence band for classical p-type semiconductors) depends on the energy level of the localized states, the temperature, and the gate voltage. However, while extended-state transport may occur in highly ordered vacuum-evaporated molecular films,[7] we do not expect it to play a role in amorphous organic films,[3] where the charge carriers are strongly localized.

In the present paper, we derive a theory for the field-effect mobility in amorphous organic transistors, where the charge transport is governed by hopping, i.e., the thermally activated tunneling of carriers between localized states, rather than by the activation of carriers to a transport level. We use the concept of variable-range hopping (VRH), i.e., a carrier may either hop over a small distance with a high activation energy or hop over a long distance with a low activation energy. The temperature dependence of the carrier transport in such a system is strongly dependent on the density of localized states. In a field-effect transistor, an applied gate voltage gives rise to the accumulation of charge in the region of the semiconducting layer that is close to the insulator. As these accumulated charge carriers fill the lower-lying states of the organic semiconductor, any additional charges in the accumulation layer will occupy states at relatively high energies. Consequently, these additional charges will—on average—require less activation energy to hop away to a neighboring site. This results in a higher mobility with increasing gate voltage.

This paper is organized as follows. First, we study the influence of temperature and the influence of the filling of states on the conductivity of a VRH system with an exponential distribution of localized-state energies. Using percolation theory, we find an analytic expression for the conductivity. This expression is then used to derive the field-effect mobility of the carriers when the material is applied in a transistor. Finally, our result is used to interpret the experimentally observed temperature and gate-voltage dependence of the field-effect mobility in both a pentacene and a polythienylene vinylene (PTV) organic thin-film transistor.[3]

Let us first derive an expression for the conductivity as a function of temperature T and charge carrier density. At low carrier densities and low T, the transport properties are determined by the tail of the density of (localized) states (DOS). Our model is based on the following exponential DOS:

$$g(\epsilon)=\frac{N_t}{k_BT_0}\exp\left(\frac{\epsilon}{k_B\,T_0}\right)\quad(-\infty<\epsilon\leqslant 0),\tag{1}$$

where N_t is the number of states per unit volume, $k_{\rm B}$ is Boltzmann's constant, and T_0 is a parameter that indicates the width of the exponential distribution. We take $g(\epsilon)=0$ for positive values of ϵ. We do not expect the results to be qualitatively different for a different choice of $g(\epsilon)$, as long as $g(\epsilon)$ increases strongly with ϵ.

Let the system be filled with charge carriers, such that a fraction $\delta\in[0,1]$ of the localized states is occupied by a

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carrier, i.e., such that the density of charge carriers is δN_t. In equilibrium, the energy distribution of the carriers is given by the Fermi-Dirac distribution $f(\epsilon,\epsilon_F)$, where ϵ_F is the Fermi energy (or chemical potential). For a given carrier occupation δ, the position of the Fermi energy ϵ_F is fixed by the condition

$$\delta=\frac{1}{N_t}\int d\epsilon\ \ g(\epsilon)f(\epsilon,\epsilon_F)$$
$$\simeq\exp\left(\frac{\epsilon_F}{k_BT_0}\right)\Gamma(1-T/T_0)\Gamma(1+T/T_0), \tag{2}$$

where $\Gamma(z)\equiv\int_0^\infty dy\ \exp(-y)y^{z-1}$. In Eq. (2), we have used the assumption that most carriers occupy the sites with energies $\epsilon\ll 0$, i.e., $-\epsilon_F\gg k_BT_0$. This condition is fulfilled when δ and T are low. Note that at $T=0$ the gamma functions are unity and the carrier density is given by the density of states with energies lower than ϵ_F. Our approximate expression (2) breaks down at temperatures $T\gtrsim T_0$, where $\Gamma(1-T/T_0)$ diverges. At such temperatures our assumption that only the tail of the DOS is important no longer holds, as the majority of the carriers is located close to $\epsilon=0$.

The transport of carriers is governed by the hopping of carriers between localized states, which is strongly dependent on the hopping distances as well as the energy distribution of the states. At low bias, the system can be described as a resistor network.[8,9] In this case, one can assign a conductance $G_{ij}=G_0e^{-s_{ij}}$ between site i and site j where

$$s_{ij}=2\alpha R_{ij}+\frac{|\epsilon_i-\epsilon_F|+|\epsilon_j-\epsilon_F|+|\epsilon_i-\epsilon_j|}{2k_BT}. \tag{3}$$

Here, the first term on the right-hand side describes the tunneling process, which depends on the overlap of electronic wave functions of the sites i and j. In a lowest-order approximation, this tunneling process may be characterized by the distance R_{ij} between the sites and an effective overlap parameter α. The second term in Eq. (3) takes into account the activation energy for a hop upwards in energy and the occupational probabilities of the sites i and j.

According to percolation theory,[9,10] the conductivity of the system is given by

$$\sigma=\sigma_0e^{-s_c}, \tag{4}$$

where σ_0 is an (unknown) prefactor and s_c is the exponent of the critical percolation conductance $G_c=G_0e^{-s_c}$. This G_c is determined as follows. Take a reference conductance G and remove all conductances with $G_{ij}<G$. For high G, the remaining conductances form isolated clusters. These clusters increase in size with decreasing G. The critical percolation conductance G_c is defined as the value of G at which the first infinite cluster is formed. This G_c determines the conductivity (4), since it is the most difficult step required for transport through a macroscopic system. The onset of percolation, i.e., the occurrence of the first infinite cluster, is usually determined by calculating the average number of bonds (conductances with $G_{ij}>G$) per site in the largest cluster. This number of bonds B increases with decreasing G, until, at the onset of percolation, a critical number B_c is reached. For a three-dimensional amorphous system, this number is given by $B_c\simeq 2.8$.[10,11] The percolation criterion $B(G=G_c)=B_c$ can be written as

$$B_c=\frac{N_b}{N_s}, \tag{5}$$

where N_b is the density of bonds and N_s is the density of sites in the percolating system. The density of bonds is given by

$$N_b=\int d\mathbf{R}_{ij}d\epsilon_id\epsilon_jg(\epsilon_i)g(\epsilon_j)\theta(s_c-s_{ij}). \tag{6}$$

The density of sites N_s can be estimated by excluding all sites that cannot possibly belong to an infinite cluster[12]

$$N_s=\int d\epsilon g(\epsilon)\theta(s_ck_BT-|\epsilon-\epsilon_F|). \tag{7}$$

Substituting Eqs. (1) and (3) into Eqs. (5), (6), and (7), we obtain the percolation criterion for our system,

$$B_c\approx\pi\left(\frac{T_0}{2\alpha T}\right)^3N_t\ \exp\left(\frac{\epsilon_F+s_ck_BT}{k_BT_0}\right), \tag{8}$$

where we have assumed that the site positions are random, that most of the hopping takes place between tail states $(-\epsilon_F\gg k_BT_0)$, and that the maximum energy hop is large $(s_ck_BT\gg k_BT_0)$. We note that our percolation criterion (8) is, up to a numerical factor, in agreement with previous results[13,14] where somewhat different approaches have been used to describe VRH in an exponential band tail.

Combining Eqs. (2), (4), and (8), the expression for the conductivity as a function of the occupation δ and the temperature T is obtained,

$$\sigma(\delta,T)=\sigma_0\left(\frac{\pi N_t\delta(T_0/T)^3}{(2\alpha)^3B_c\Gamma(1-T/T_0)\Gamma(1+T/T_0)}\right)^{T_0/T}. \tag{9}$$

Note that the conductivity has an Arrhenius-like temperature dependence $\sigma\sim\exp[-E_a/(k_BT)]$, with an activation energy E_a that is weakly (logarithmically) temperature dependent. This is in strong contrast with the well-known Mott formula for VRH in a constant DOS, where $\sigma\sim\exp[-(T_1/T)^{1/4}]$.[15] The temperature dependence of the Mott formula is a consequence of hopping over far distances and hopping to high energies being equally important. In an exponential DOS, however, the characteristic hop is an activated jump, since there are much more available states at higher energies. In fact, it has been shown that hopping in an exponential DOS can be effectively described in terms of activation from the Fermi energy to a specific transport energy.[16,17] This explains the Arrhenius behavior of Eq. (9).

In our expression (9), the conductivity increases superlinearly with the density of carriers ($\sigma\sim\delta^{T_0/T}$). This is due to the filling of localized states: an increase in the carrier density gives rise to an increase in the average energy, thus facilitating an activated jump to the transport energy mentioned above. When the filling of states is not taken into account, i.e., when Boltzmann statistics instead of Fermi-

Dirac statistics is used in Eq. (2), the conductivity is simply proportional to the density of carriers.[13,14]

We now apply the obtained conductivity (9) to describe the field-effect mobility μ_{FE} in a transistor. In bulk material, the mobility μ of the charge carriers is given by $\mu = \sigma(\delta,T)/(e\delta N_t)$. In a transistor, however, the charge density is not uniform, but it decreases with the distance x from the semiconductor-insulator interface. According to Eq. (2), the occupation $\delta(x)$ depends on the distance x through the gate-induced potential $V(x)$,

$$\delta(x)=\delta_0 \exp\left(\frac{eV(x)}{k_B T_0}\right), \tag{10}$$

where δ_0 is the carrier occupation far from the semiconductor-insulator interface, where $V(x)=0$. The variations of $V(x)$ and $\delta(x)$ with the distance x are determined by the Poisson equation. For the accumulation layer, where $\delta(x)\gg\delta_0$, the following relation between the electric field $F(x)=-dV(x)/dx$ and $\delta(x)$ can be obtained,[7]

$$F^2(x)=2k_B T_0 N_t \delta(x)/\epsilon_s, \tag{11}$$

where ϵ_s is the dielectric constant of the semiconductor. The field $F(0)$ at the interface can be expressed in terms of the gate voltage V_G and and the insulator capacitance per unit area C_i through Gauss' law,

$$F(0)=C_i V_G/\epsilon_s. \tag{12}$$

Substituting the distance-dependent charge occupation $\delta(x)$ into Eq. (9) for the conductivity, the source-drain current of the transistor in the linear regime $(-V_D < -V_G)$ reads

$$I=\frac{WV_D}{L}\int_0^t dx\,\sigma[\delta(x),T]. \tag{13}$$

Here, V_D is the drain voltage (the source is the ground electrode) and L, W, and t are the length, width, and thickness of the channel, respectively. The field-effect mobility then follows from the transconductance (see, e.g., Ref. 3):

$$\mu_{\mathrm{FE}}\equiv\frac{L}{C_i W V_D}\frac{\partial I}{\partial V_G}. \tag{14}$$

From Eqs. (9)–(14) we obtain the following expression for the field-effect mobility,

$$\mu_{\mathrm{FE}}=\frac{\sigma_0}{e}\left(\frac{\pi(T_0/T)^3}{(2\alpha)^3 B_c \Gamma(1-T/T_0)\Gamma(1+T/T_0)}\right)^{T_0/T} \times\left[\frac{(C_i V_G)^2}{2k_B T_0 \epsilon_s}\right]^{T_0/T-1}, \tag{15}$$

where we have assumed that the thickness t of the semiconductor layer is sufficiently large such that $V(t)=0$. Then the field-effect mobility is independent of the thickness t as well as the bulk carrier occupation δ_0. We note that the N_t dependence of the charge distribution in the accumulation layer is exactly canceled by the N_t dependence of $\sigma(\delta,T)$.

Let us now apply our result (15) to the experimental data of Ref. 3, where the drain current I versus gate voltage V_G characteristics have been measured of both a pentacene and a polythienylene vinylene (PTV) organic thin-film transistor at a range of temperatures. The precursors of both organic semiconductors are spin coated from solution on a substrate consisting of a heavily n-doped silicon (common) gate electrode, a 200 nm thick SiO_2 insulating layer ($C_i=17$ nF cm^{-2}), and a patterned gold layer as the source and drain electrodes. The precursors are converted into the organic semiconductors using a process described in Ref. 3. Typical channel widths and lengths were $W=10$–20 mm and $L=2$–20 μm, respectively. The film thickness t varied from 30 to 50 nm. For both semiconductors, we use a relative dielectric constant $\epsilon_r=3$, which is appropriate for most organic solids. In Fig. 1 the field-effect mobility in a pentacene and in a PTV thin-film transistor is plotted against the inverse temperature for different gate voltages. Experimentally, the field-effect mobilities are determined from Eq. (14) at $V_D=-2$ V. The theoretical curves (solid lines) follow from Eq. (15), where we have used σ_0, α, and T_0 as fitting parameters. The agreement with experiment is quite good (the parameter values are given in Table I). The temperature dependence of μ_{FE}, as shown in Fig. 1, follows a simple Arrhenius behavior $\mu_{\mathrm{FE}}\sim\exp[-E_a/(k_B T)]$, where the activation energy E_a depends on V_G as plotted in Fig. 2. The decrease of E_a with increasing (negative) gate voltage is the direct result of accumulated charges filling the lower-lying

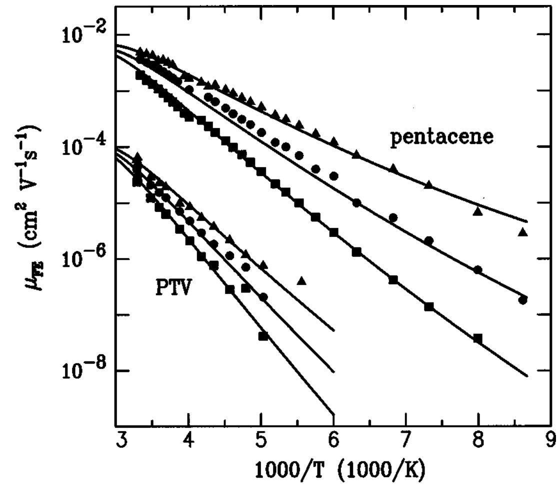

FIG. 1. Field-effect mobility μ_{FE} in a pentacene and a polythienylene vinylene (PTV) thin-film transistor as a function of the temperature T for different gate voltages $V_G=-20$ V (triangles), -10 V (circles), and -5 V (squares). The experimental data (symbols) are taken from Ref. 3. The solid lines are according to Eq. (15), using the parameters given in Table I.

TABLE I. The preexponential factor to the conductivity σ_0, the overlap parameter α^{-1}, and the width of the exponential distribution of localized states T_0 for both pentacene and polythienylene vinylene (PTV) as obtained from the fit of Eq. (15) to the experimental data of Ref. 3, see Fig. 1.

	σ_0(10^{10} S/m)	α^{-1} (Å)	T_0 (K)
Pentacene	1.6	2.2	385
PTV	0.7	0.8	380

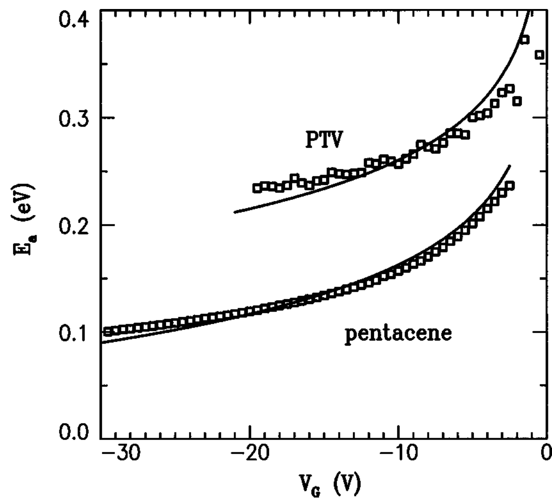

FIG. 2. Activation energy E_a for the field-effect mobility in a pentacene and a polythienylene vinylene (PTV) thin-film transistor as a function of the gate voltage V_G. The experimental data (squares) are taken from Ref. 3. The solid lines are calculated from Eq. (15), using the parameters given in Table I.

states. As a result, any additional charge carriers in the system will occupy sites with—on average—a higher energy and less energy will be required for the activated jumps to neighboring sites.

The field-effect mobility in PTV is more than two orders of magnitude lower than the field-effect mobility in pentacene. Furthermore, the activation energy for PTV is about twice the activation energy for pentacene. Surprisingly, these differences cannot be attributed to differences in the prefactor σ_0 nor to the width of the energy distribution T_0, as these parameters have similar values for PTV as well as pentacene (see Table I). The main difference between pentacene and PTV appears to be in the overlap parameter α, which determines the tunneling process between different sites. We note that this key parameter is absent in a multiple-trapping model, where the transport is governed by thermal activation from traps to a conduction band and subsequent retrapping, without involving a tunneling step. As the length scale α^{-1} is smaller than the size of a molecule, one must be cautious not to interpret α^{-1} simply as the decay length of the electronic wave function. The size and shape of the molecules and the morphology of the organic film are expected to have an important influence on the tunneling probability as well. The observed difference in α^{-1} may be due to the fact that there is more steric hindrance in the polymer PTV than in a system of small pentacene molecules. The better stacking properties of pentacene give rise to a larger area of overlap of the electronic wave functions, which results in a larger effective overlap α^{-1} in our model.

In conclusion, we have derived an analytic expression for the field-effect mobility in a thin-film transistor of an amorphous organic semiconductor, using percolation theory and the concept of hopping in an exponential density of localized states. The calculated temperature dependence and gate-voltage dependence agree well with those of the the observed field-effect mobility in both a pentacene and a PTV thin-film transistor. According to the theory, the differences in the magnitude and in the temperature dependence of the field-effect mobility of pentacene and PTV transistors are mainly due to differences in the structural order of the organic films.

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