Effect of microscopic Coulomb interactions on concentration dependence mobility of charge carriers in organic materials

V R Nikitenko and A Yu Saunina
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, 115409, Russia

*Corresponding author’s e-mail address: vladronik@yandex.ru

Abstract. The filling of deep states is considered usually to be the reason of increase of the mobility of disordered organic materials with increasing concentration. However, at moderate concentrations the effect of microscopic Coulomb interactions (MCI) could be significant, because these interactions can reduce the activation energy of a hop. It is shown, that MCI results in significant additional increase of mobility along with concentration, in addition to the effect of the filling of deep states. The results are in qualitative agreement with existing theoretical and experimental studies.

1. Introduction
The mobility of charge carriers is one of the most important characteristics of transport. In recent years, considerable attention is paid to experimental [1] and theoretical [2-6] studying of transport in disordered organics in case, where the effect of charge carrier concentration on the mobility is significant. It was shown, that the mobility is increasing significantly with increasing concentration. This dependence is essential for organic field-effect transistors, where the relative concentrations could reach the value of 0.01 [1], but in case of ohmic contacts it should be also taken into account for organic light-emitting diodes, although the concentration values there are much lower.

The filling of deep states is considered to be the main reason of increase of the mobility with increasing concentration. In that case these states stop acting as “traps”. This mechanism is studied in a couple of works, see for example [2-6]. However, at moderate concentrations the other effect could be more significant – strong Coulomb repulsion of randomly nearing charges, which accelerates the release of charges from deep states. This effect is considered in present work analytically.

2. Model for mobility calculation considering microscopic Coulomb interactions
Transport in organic materials occurs due to hopping of charge carriers between localized states, randomly distributed in energy [2,7,8]. Consider a carrier (a test charge), jumping on a typical distance $\Delta r$ (in proximity to average distance between hopping centers). Energy of Coulomb interaction between the test charge and neighboring charges of the same sign, $\Delta U$, varies randomly after a hop, since the direction of the hop is subjected to random scattering. The effect of the nearest neighbour, located at a distance $r$, is only significant at moderate carrier concentrations. The value of microscopic Coulomb field, $F = e/\kappa r^2$, where $\kappa = 4\pi\varepsilon\varepsilon_0$, is approximately uniform, hence it is proportional to variation of potential energy $\Delta U$, since $\Delta r/r \ll 1$:
\[ \Delta U = \frac{e^2}{\kappa |r|} - \frac{e^2}{\kappa |r| + \Delta r} \approx eF \Delta r \cos \theta + \Delta U^{(2)} \approx eF_0 \Delta r , \] (1)

where \( \theta \) - the angle between field and jump directions, \( F_0 \) is a projection of electric field on the direction of a jump. The term \( \Delta U^{(2)} \approx eF \Delta r^2 / r \) is negligible compared to thermal energy \( kT \), if \( c << c_{\text{max}} \approx N_0^{(-1/3)} / r \), considering \( \Delta r \approx N_0^{(-1/3)} \) \( (r_c = e^2 / kT \) is a Coulomb radius). The estimation at room temperature, \( e = 3 \), \( N_0 \approx 10^{21} \text{ cm}^{-3} \) gives \( c_{\text{max}} \approx 0.01 \). On the other hand, microscopic Coulomb interactions (MCI) could affect significantly the release rates from deep states (and, consequently, the mobility), providing that \( \Delta U > kT \). Considering eq. (1), one obtains

\[ \left( N_0^{(-1/3)} / r \right)^{3/2} < c_{\text{max}} . \]

Apparently, in this approximation \( \Delta U \) is nothing but interaction energy between the test charge and small-size dipole \( \vec{p} = e \Delta \vec{r} \), situated on a distance \( r \) from it, see Figure. 1.

\[ \left( \frac{2}{2^3} \right) \exp \left( - \frac{4 \pi}{3} N_0 e^3 \right) . \]

where \( A \) - normalization factor. Moving from potential energy to module of electric field strength in eq. (2), one gets the following distribution function with normalization factor \( C_F \).
The function $\Phi(F_0, c)$ contains the parameter $c$, the relative concentration of carriers, as well as the function $w$. Consider uniform external electric field $E_x$, directed along the $x$ axis, in order to calculate mobility. Note, that mobility in materials with strong Gaussian disorder is defined by release of carriers from relatively deep states with typical energies of $-\sigma^2/kT$, $\sigma/kT >> 1$, if $c < c_c$, or from states near quasi-Fermi level, if $c > c_c$. The initial state is assumed to be deep enough in order to the jump in any direction being thermally activated. In the presence of both external and microscopic fields, the activation energy is changing by some value $\Delta U = U(\tilde{E}_x, F_0)$. Typical release rate could be written as: $\nu(c) = \nu_0(c) \exp(\Delta \tilde{U}/kT)$, where $\nu_0$ corresponds to zero field strength (however, it depends on relative concentration, $c$). The mobility is calculated as average drift velocity in single external field:

$$\mu(c, F_\sigma) = \frac{(v_{\Delta x})}{E_x} = \int_{-\infty}^{\infty} dF_0 \Phi(F_0, c) \left[ \frac{\nu_0(c)(\Delta x)(F_0)}{E_x} \int_{-\infty}^{\infty} d\tilde{U} G(\tilde{E}_x, F_\sigma, F_0) e^{\tilde{U}/T} \right],$$

(5)

where $G(\tilde{U}, F_\sigma, F_0)$ is a distribution function of energy $U_{\sigma}$, which, in general, includes $F_\sigma$ and $F_0$ as parameters. The analysis of this function is beyond the scope of this work. According to eq. (5), the mobility dependence on concentration could be determined by averaging of “local” mobility $\mu(F_0, c)$, see the expression in square brackets, which is calculated at a certain microscopic field $F_\sigma$, with distribution function $\Phi(F_0, c)$. In the case of rather weak external field, one can neglect the dependence of mobility on that field,

$$\mu(c) = \int_{0}^{\infty} dF_0 \Phi(F_0, c) \mu(F_0, c).$$

(6)

The local carrier mobility $\mu(F_0, c)$ is calculated according to model, based on percolation theory [10,11]:

$$\mu(F_0, c) = \frac{\nu_0}{c} \exp \left[ -\frac{E_c(F_0) - E_r(c)}{kT} \right].$$

(7)

Here, the transport level $E_c$ dependence on field strength $F_0$ yields well-known phenomenological, so called Pool-Frenkel field dependence of mobility, and is in accord with correlated disorder theory by Novikov et al. [12]:

$$E_c(F_0) = E_{c_0} + kT \varphi \sqrt{F_0}, \quad \varphi = \tilde{C} \left[ (\sigma/kT)^{1/2} - \Gamma \right],$$

(8)

where $E_{c_0}$ is an effective transport level in a low field limit [13], $\tilde{C} = 8.85 \cdot 10^{-5} (\text{m/V})^{1/2}$ and $\Gamma = 2$.

3. Results and Discussion

Results of calculations of mobility dependence on concentration in a weak external electric field in comparison with experimental data (from well-known work [1]) and with results of Extended Gaussian Disorder Model (EGDM) [2] for two different values of disorder parameter are shown in Figures. 2 and 3. Note, that the experimental results (see empty symbols) cover only the low and the high...
concentrations regions. The used values of parameters $\Delta r = 1.2 \text{ nm}$, $2\gamma \Delta r = 10$ - are in proximity to those used in the work [1] for analysis of experimental data. The qualitative agreement with the experimental data is achieved by the use the same values in eq. (8), as in the ref. [12].

Figure. 2 shows, that the model considering MCI gives result in qualitative agreement with experimental data (except of very high concentrations region), whereas other models do not provide sufficient mobility increase, at moderate value of disorder parameter, $\sigma / kT = 4$.

**Figure 2.** Concentration dependence of mobility in a weak external electric field for disorder parameter $\sigma / kT = 4$. Empty squares presents experimental data [1]. Full squares shows results of calculations according to eq. (7) considering MCI, see. eqs. (3)-(6), while the solid line is the same non considering MCI. Results of Extended Gaussian Disorder Model (EGDM) [2] are shown by line with symbols.

**Figure 3.** The same as in fig. 2, but $\sigma / kT = 6$. 

![Figure 2 Image](image-url)  
![Figure 3 Image](image-url)
The conclusion about quantitative agreement in moderate concentrations region (from $10^{-5}$ to $10^{-3}$) could not be made due to the lack of experimental results in that region. The discrepancy between MCI model and the experimental data at high concentrations ($c > 0.01$) is not surprising, since the approximation (1) in this region is not applicable, and one need take into account not only the effect from the nearest neighbor, but also from other neighboring charges. From the Figure 3 one can notice, that with large disorder parameter ($\sigma / kT = 6$, that gives $\sigma = 0.15$ at room temperature, proximal to $\sigma = 0.14$, used in [2]), good fit is obtained at moderate and high concentrations without considering MCI, while MCI provide too strong increase of mobility in this case. However, models not considering MCI provide too small mobility in limiting case of low concentrations, than the experiment.

4. Conclusion

Theoretical model of mobility dependence on carrier concentration in disordered organic materials at weak electric field, considering not only the filling of deep “tale” of DOS, but also Coulomb interactions between randomly nearing charges, was built. Microscopic Coulomb interactions (MCI) results in considerable increase of mobility at moderate concentrations, if the field dependence of mobility is rather strong. Previously, the effect of MCI (“short-range Coulomb interactions”) on J-V characteristics (not directly on mobility) was studied by the means of Monte-Carlo modelling, and considerable reduction of current, at low voltages and small layer thickness, was demonstrated [14]. One has to note, that it is hard to distinguish effects of MCI on transport and injection in the case of thin (22 nm) layer and low (about 0.1 V) voltage [15]. Thus, further investigations are necessary. The analytic treatment of MCI in the present work do not claim to quantitative accuracy, being only the upper estimation, since only the interaction with the nearest charge of the same sign is considered. One has to stress, that various sets of parameters could be derived from analyses of experimental data, considering or not considering MCI. One of the aims of this work is to get the attention to a problem of independent (apart from J-V characteristics measurements) and reliable definition of disorder parameter, $\sigma / kT$, in order to validate one or another model of field dependence of the mobility, and to make conclusions about the effect of MCI on concentration dependence, using experimental concentration dependence of mobility.

References

[1] Tanase C, Blom P W M, de Leeuw D M and Meijer E J 2004 Charge carrier density dependence of the hole mobility in poly(p-phenylene vinylene) Physica Status Solidi a-Applied Research 201 1236
[2] Pasveer W F, Cottaar J, Tanase C, Coehoorn R, Bobbert P A, Blom P W M, de Leeuw D M and Michels M A J 2005 Unified description of charge-carrier mobilities in disordered semiconducting polymers Physical Review Letters 94 206601
[3] Oelerich J O, Huemmer D, Weseloh M and Baranovskii S D 2010 Concentration dependence of the transport energy level for charge carriers in organic semiconductors Applied Physics Letters 97 143302
[4] Zvyagin I P 2008 A percolation approach to the temperature and charge carrier concentration dependence of the hopping conductivity in organic materials Physica Status Solidi C - Current Topics in Solid State Physics 5 725
[5] Cottaar J, Coehoorn R and Bobbert P A 2012 Scaling theory for percolative charge transport in molecular semiconductors: Correlated versus uncorrelated energetic disorder Physical Review B 85 245205
[6] Li L, Lu N, Liu M and Bassler H 2014 General Einstein relation model in disordered organic semiconductors under quasi-equilibrium Physical Review B 90 214107
[7] Bassler H 1993 Charge transport in disordered organic photoconductors - a Monte-Carlo simulation study Physica Status Solidi B-Basic Research 175 15
[8] Baranovskii S D 2014 Theoretical description of charge transport in disordered organic semiconductors Physica Status Solidi B-Basic Solid State Physics 251 487
[9] Novikov S V 2008 Thesis (Moscow: IPCE RAS)
[10] Shklovskii V I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (Berlin: Springer)
[11] Cottaar J, Koster L J A, Coehoorn R and Bobbert P A 2011 Scaling Theory for Percolative Charge Transport in Disordered Molecular Semiconductors *Physical Review Letters* **107** 136601
[12] Novikov S V, Dunlap D H, Kenkre V M, Parris P E and Vannikov A V 1998 Essential role of correlations in governing charge transport in disordered organic materials *Physical Review Letters* **81** 4472
[13] Nikitenko V R and Strikhanov M N 2014 Transport level in disordered organics: An analytic model and Monte-Carlo simulations *Journal of Applied Physics* **115** 073704
[14] van der Holst J J M, van Oost F W A, Coehoorn R and Bobbert P A 2011 Monte Carlo study of charge transport in organic sandwich-type single-carrier devices: Effects of Coulomb interactions *Physical Review B* **83** 085206
[15] Nikitenko V R, Sannikova N A and Strikhanov M N 2014 Features of the Current-Voltage Characteristics in Thin Conductive Layers of Organic Light-Emitting Diodes *Semiconductors* **48** 1494