A hopping transport model based on the effective temperature for disordered organic semiconductors

Z. P. KOU, L. G. WANG*, M. L. LIU, Y. F. LI, L. ZHANG
School of Electrical Engineering and Automation, Henan Key Laboratory of Intelligent Detection and Control of Coal Mine Equipment, Henan Polytechnic University, Jiaozuo, 454003, People's Republic of China

The theoretical description of effect of the electric field on the mobility belongs to the not-yet-resolved problem related to charge transport in disordered organic semiconductors. Recently, the extended Gaussian disorder model (EGDM), a widely used mobility function, is heavily criticized for an underestimation of the electric field dependence of the mobility. In this paper, we propose an improved effective temperature extended Gaussian disorder model (ET-EGDM) by inserting the field dependent effective temperature instead of the real temperature into the EGDM. The improved model is applied to temperature dependent current density-voltage characteristics of hole-only and electron-only devices based on polymer:non-fullerene PM6:Y6 blend. In contrast to the EGDM, the improved model provides a better description of charge transport in PM6:Y6 blend, especially for electron-only device. The extracted values of intersite distance from the ET-EGDM are obviously smaller than that from the EGDM for both hole-only and electron-only devices, indicating that the ET-EGDM predicts a much stronger electric field dependence than the EGDM. These results prove that the effective temperature, responsible for the combined effects of the electric field and real temperature on the hopping mobility.

(Received September 30, 2023; accepted April 10, 2024)

Keywords: Charge transport, Mobility model, Effective temperature, Disordered organic semiconductors

1. Introduction

Disordered organic semiconductors play a central role in the active layer of various types of organic optoelectronic devices, such as organic light emitting diodes, organic field effect transistors, and organic photovoltaic devices [1-5]. The term disordered organic semiconductors covers a large class of materials, which can essentially differ from each other in morphology and chemical composition. Most prominent representatives of disordered organic semiconductors are molecularly doped polymers, conjugated polymers, and low-molecular-weight materials. Physical insight of charge carrier transport in these materials is vital for understanding the operating mechanisms of organic electronic devices [6-8]. A difficult task is to theoretically interpret the hopping transport process between the localized states in these materials.

For disordered organic semiconductors, charge carrier transport is commonly understood to occur via incoherent thermally activated tunneling (hopping) of charge carriers between randomly distributed localized states with a Gaussian energy spectrum. The most important parameter characterizing charge transport is the carrier mobility μ. Understanding the effect of disorder on the dependence of the mobility on temperature T, electric field F and carrier concentration p is crucial for modeling the electronic processes in disordered organic semiconductors. Various approaches have been proposed to calculate the mobility functional, $\mu(T, p, F)$, for hopping transport in disordered organic semiconductors. Seminal work by Bässler et al. used kinetic Monte Carlo simulations, the random energies were described by a Gaussian density of states (DOS) [9, 10], leading to the Gaussian disorder model (GDM). This model provides a description of the temperature dependence of the mobility for vanishing carrier concentration, and shows discrepancies in the field dependence that are attributed to spatial correlations of the site energies [11, 12]. Later, it was realized that, apart from the dependence of μ on temperature T and electric field F, there is a strong dependence on the carrier concentration p [13-17]. Based on a numerically exact approach, a parametrization scheme for the corresponding mobility functional $\mu(T, p, F)$ was constructed by Pasveer et al., which is known as the extended Gaussian disorder model (EGDM) [15]. Although this mobility model is conveniently implemented in drift-diffusion solvers and is widely used, it is also heavily criticized [18-20]. A major point of criticism is the assumption of a regular cubic lattice and the use of a small and constant localization radius that enforces strict nearest neighbor hopping (NNH) and gives rise to an underestimation of the electric field F dependence of the mobility μ [19]. A strongly related problem is the absence of a complementary variable-range hopping (VRH) model for a Gaussian density of states. It is therefore important to account for the VRH regime theoretically studying charge transport in disordered

organic semiconductors. To date, the state of research related to the theoretical description of charge transport in disordered organic semiconductors can hardly be considered as satisfactory.

In this paper, we propose an improved effective temperature extended Gaussian disorder model (ET-EGDM) by inserting the field dependent effective temperature instead of the real temperature into the EGDM. As an application of our results, we analyze the temperature dependent current density-voltage ($J - V$) characteristics of hole-only and electron-only devices based on polymer:non-fullerene PM6:Y6 blend by using the ET-EGDM. For the device studied, a very good description of the J - V characteristics can be obtained within the ET-EGDM, but with a much smaller intersite distance than obtained within the description using the EGDM. These results show that the ET-EGDM predicts a much stronger electric field dependence than the EGDM, the effective temperature responsible for the combined effects of the electric field and real temperature on the hopping mobility.

2. Models

It is widely accepted that charge transport in most disordered organic semiconductors is due to incoherent tunneling (hopping) of charge carriers between localized states that are randomly distributed in space. The most popular charge transport model in disordered organic semiconductors is the Gaussian disorder model (GDM), according to which localized states have a Gaussian energy distribution [9, 21]

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right) \tag{1}$$

Here, σ is the energetic disorder of the density of states (DOS), usually estimated in disordered organic semiconductors to the order of $\sigma \approx 0.1$eV, and N is the concentration of localized states that is related to the mean intersite distance (lattice constant) by $a = N^{-1/3}$.

The charge hopping rates are usually assumed to be described by the Miller-Abrahams expression [22]. In their model the rate of carrier hopping from site i to an unoccupied site j, that is V_{ij}, depends on the spatial distance R_{ij}, and the energetic difference between the sites $\Delta\varepsilon = \varepsilon_j - \varepsilon_i$, and was calculated as:

$$V_{ij} = \nu_0' \exp\left(\frac{-2R_{ij}}{\alpha}\right) \exp\left(-\frac{\Delta\varepsilon}{k_B T}\right) \tag{2}$$

Here, α is the localization length of the charge carriers on the sites, k_B is the Boltzmann constant, $\Delta\varepsilon = \max(0, \varepsilon_j - \varepsilon_i - \vec{F}\cdot\vec{r}_{ij})$, F is the local electrostatic field vector, and r_{ij} is the vector from i to j. The prefactor $\nu_0' = \nu_0 \exp(2a/\alpha)$ make ν_0' become the rate of downward hops to a nearest neighbor site, and ν_0 is typically identified as the attempt-to-hop frequency.

Numerical solutions for the charge carrier mobility and current density in disordered organic systems, with rates given by Eq. (2) and site energies randomly drawn from Eq. (1), have been reported by various authors. In the pioneering work of Bässler and Borsenberger et al., they numerically simulated the dependencies of μ on temperature T and electric field F in a system of sites placed on a simple cubic lattice and fitted the numerical results by the parameterized equation [9, 10].

$$\mu_{GDM}(T, F) = \mu_0 \exp\left[-\left(\frac{2}{3}\hat{\sigma}\right)^2 + C\left(\hat{\sigma}^2 - \Sigma^2\right)\sqrt{F}\right] \tag{3}$$

with $\hat{\sigma} \equiv \sigma / k_B T$, μ_0 is a field independent prefactor, Σ is a parameter describing the off-diagonal disorder, and C is an empirical constant depending on the distance between the hopping sites. Eq. (3) is one of the most widely used equations in the context of organic semiconductors.

A similar approach to determine mobility function was put forward by Pasveer et al. [15], who reduced the lattice GDM of Bässler et al. to the case $\Sigma = 0$ and herewith completely eliminated the spatial disorder. In the framework of this reduced GDM on a simple cubic lattice with uncorrelated Gaussian disorder, a full description of the mobility taking into account both the field and charge carrier density dependence was obtained by Pasveer et al. in the form of the extended Gaussian disorder model (EGDM) [15]. In the EGDM the mobility can be expressed as

$$\mu(T, p, F) = \mu(T, p) f(T, F) \tag{4}$$

with $\mu(T, p)$ and $f(T, F)$ in the form:

$$\mu(T, p) = \mu_0(T) \exp\left[\frac{1}{2}\left(\hat{\sigma}^2 - \hat{\sigma}\right)\left(2pa^3\right)^{\delta}\right] \tag{5}$$

$$f(T, F) = \exp\left\{0.44\left(\hat{\sigma}^{3/2} - 2.2\right)\left[\sqrt{1 + 0.8\left(\frac{eaF}{\sigma}\right)^2} - 1\right]\right\} \tag{6}$$

where $\mu(T, p)$ and $f(T, F)$ are density dependent and field dependent factor, respectively. The EGDM is sometimes considered universal, and is the basis for commercially available organic devices simulation software [23]. However, the methodology followed to derive the above GDM and EGDM parametrizations has been heavily criticized for giving an inadequate description of especially the field dependence of the mobility [18-20].

A milestone for the theoretical description of the dependence $\mu(F)$ in materials with hopping transport

was set by Shklovskii for the case $T = 0$, who recognized that the effect of the electric field F on the carrier mobility μ is determined by the product $eF\alpha$ (α is the localization length) [24]. For the case $T \neq 0$, Shklovskii and successors argued that the combined effects of the electric field F and temperature T on the hopping mobility can be expressed in the form of an effective temperature [25, 26]:

$$T_{eff} = \left[T^2 + (\gamma \frac{eF\alpha}{k_B})^2 \right]^{1/2} \tag{7}$$

With $\gamma \approx 0.67$. The validity of the approach based on the effective temperature has been confirmed in numerous studies [18-20].

In principle, Eq. (7) can be combined with any model that describes the temperature dependent mobility of a hopping system by replacing the temperature T by an effective temperature T_{eff}. To describe the combined effects of electric field and temperature on the hopping mobility, we will improve the EGDM expression by inserting the field dependent effective temperature T_{eff}, instead of the real temperature T, into the temperature dependence of the hopping mobility:

$$\mu(T, p, F) = \mu(T_{eff}, p) f(T_{eff}, F) \tag{8}$$

where

$$\mu(T_{eff}, p) = \mu_0(T_{eff}) \exp[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^{\delta}] \tag{9}$$

$$f(T_{eff}, F) = \exp\left\{ 0.44\left(\hat{\sigma}^{3/2} - 2.2\right)\left[\sqrt{1 + 0.8\left(\frac{eaF}{\sigma}\right)^2} - 1 \right] \right\} \tag{10}$$

$$\mu_0(T_{eff}) = \mu_0 c_1 \exp(-c_2 \hat{\sigma}^2) \tag{11}$$

$$\delta \equiv 2\frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2}, \quad \mu_0 \equiv \frac{a^2 \nu_0 e}{\sigma} \tag{12}$$

In the following, the mobility model Eqs.(8)-(12) will be referred to as the effective temperature extended Gaussian disorder model (ET-EGDM).

3. Results and discussion

Recent progress in bulk-heterojunction organic solar cells (OSCs) was dominated by the development of non-fullerene acceptor materials. A novel non-fullerene acceptor material developed by Zou et al. is named Y6, which includes ladder-type electron-deficient-core-based central fused ring [27]. By coupling Y6 with PM6, the authors were able to make a breakthrough and demonstrate high power conversion efficiency (PCE) up to 15.7%. This combination of PM6 and Y6 results in efficient optimization of all the parameters. Despite the progress in the PCE, only limited research has been performed on charge transport in polymer:non-fullerene blends. Charge transport directly impacts the performance of solar cells, while the hole and electron transport may also be relevant to exciton diffusion. It would be very interesting to have further investigations of the processes related with charge transport in this material combination. It is important that the proposed ET-EGDM model can provide a consistent description of charge transport in polymer:non-fullerene blends. In addition, reliable disorder values for these polymer:non-fullerene blends are rare.

Figure 1 shows the analysis of hole-only device of the amorphous polymer:non-fullerene PM6:Y6 blend, using mobilities from both the EGDM and ET-EGDM models. The dashed lines and solid lines represent the numerically calculated results from the EGDM and ET-EGDM model, respectively. The symbols are the experimental data from Ref. [28]. It can be seen from the figure that the temperature dependent J - V characteristics of hole-only device based on PM6:Y6 blend can be well described by both models using three fit parameters, σ = 0.1 eV, a = 1.9 nm, μ_0 = 5000 m^2/Vs and σ = 0.1 eV, a = 1.2 nm, μ_0 = 3388 m^2/Vs for the EGDM and ET-EGDM, respectively. Here, σ mainly controls the temperature dependence, whereas a predominantly affects the field dependence and μ_0 controls the magnitude of the mobility. For hole-only device, there is no noticeable difference in fit quality, and the extracted disorder values of σ for the EGDM and ET-EGDM models are the same. However, the extracted values of intersite distance (lattice constant) for the both models are quite different. The value of a from the ET-EGDM is obviously smaller than that from the EGDM, indicating that the ET-EGDM predicts a much stronger F dependence than the EGDM.

We further consider the question whether the proposed ET-EGDM model also provides a consistent description of electron transport in PM6:Y6 blend. When the EGDM and ET-EGDM models are also applied to electron-only device based on PM6:Y6 blend, it is not difficult to find in Fig. 2 that the influence of effective temperature T_{eff} on the J - V characteristics is more notable in comparison with that in hole-only device. The temperature dependent J - V characteristics of electron-only device based on PM6:Y6 blend can also be well described by both models using three fit parameters, σ = 0.09 eV, a = 2.1 nm, μ_0 = 2500 m^2/Vs and σ = 0.085 eV, a = 1.3 nm, μ_0 = 1355 m^2/Vs for the EGDM and ET-EGDM, respectively. By comparing the fit quality from the EGDM and ET-EGDM, we can find that the numerically calculated results from the ET-EGDM are more consistent with experimental data than the EGDM, especially at low voltage. For electron-only device, the extracted disorder values of σ for the EGDM and ET-EGDM are rather similar. However, similar to hole-only device, the extracted disorder value of a from the ET-EGDM is obviously smaller than that from the EGDM, further indicating that the ET-EGDM predicts a much stronger F dependence than the EGDM.

It can be seen from Fig.1 and Fig.2 that both the EGDM and ET-EGDM models excellent fits to the temperature dependent *J* - *V* characteristics of PM6:Y6 hole-only and electron-only devices can be obtained. There is no significant difference in the fit quality for hole-only device. However, the numerically calculated results from the ET-EGDM are more consistent with experimental data than the EGDM for electron-only device. The extracted disorder values of σ for the EGDM and ET-EGDM models are rather similar for both hole-only and electron-only devices. Intuitively, on the basis of low energy loss in OSC system, one might expect a relatively small energetic disorder [27, 29]. However, we find σ = 0.1 eV for hole-only device and σ = 0.09 eV and 0.085 eV for electron-only device, which would correspond to a disorder-induced voltage loss in excess of 0.2 V [30]. Although this is beyond the scope of the present work, we note that the high PCE values observed for this system are unlikely to be related to a suppressed energetic disorder. What's more, it is worth noting that the extracted value of a from the ET-EGDM is obviously smaller than that from the EGDM for both hole-only and electron-only devices. From the above results, it can be concluded that the ET-EGDM predicts a much stronger electric field dependence than the EGDM, the effective temperature responsible for the combined effects of the electric field and real temperature on the hopping mobility.

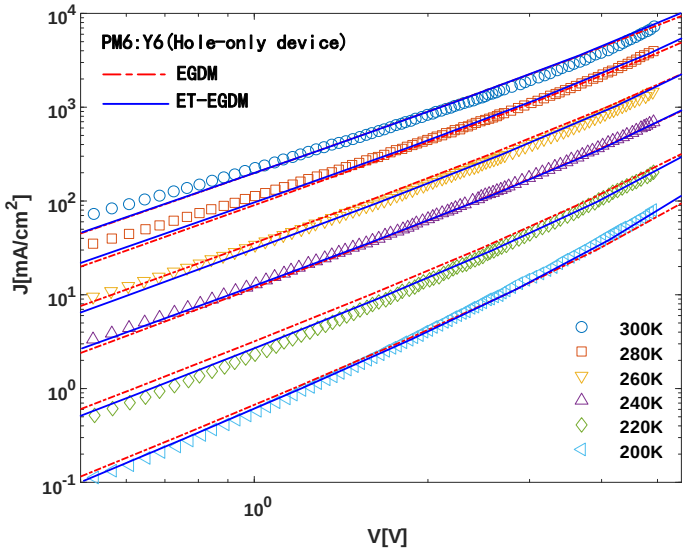

Fig. 1. Temperature dependent $J-V$ characteristics of PM6:Y6 hole-only device. Symbols are experimental data from Ref. [28]. The dashed lines and solid lines represent the numerically calculated results from the EGDM and ET-EGDM model, respectively (color online)

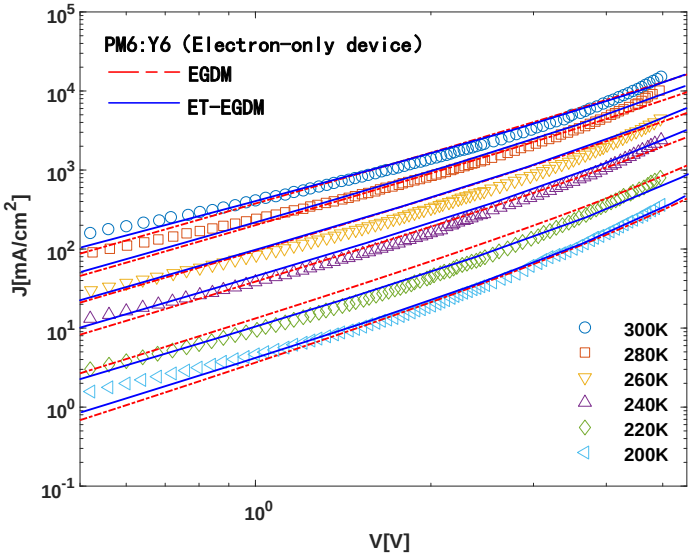

Fig. 2. Temperature dependent $J-V$ characteristics of PM6:Y6 electron-only device. Symbols are experimental data from Ref. [28]. The dashed lines and solid lines represent the numerically calculated results from the EGDM and ET-EGDM model, respectively (color online)

4. Summary and conclusions

In conclusion, we present an improved effective temperature extended Gaussian disorder model for charge transport in disordered organic semiconductors. Analysis of experimental temperature dependent *J* - *V* characteristics shows that the improved model can adequately describe hole and electron transport in polymer:non-fullerene PM6:Y6 blend, which is one of the currently best performing binary systems in organic solar cells field. The extracted value of intersite distance from the ET-EGDM is obviously smaller than that from the EGDM for both hole-only and electron-only devices, indicating that the ET-EGDM predicts a much stronger electric field dependence than the EGDM. These results show that the dependence of the carrier mobility on the electric field can be described by inserting the effective temperature, instead of the real temperature, into the temperature dependence of the mobility.

Acknowledgements

This work is supported by the Natural Science Foundation of Henan Province Grant No. 242300420282 and No. 242300420685, the Fundamental Research Funds for the Universities of Henan Province Grant No. NSFRF240818, No. NSFRF240712 and No. NSFRF200304, the Science and Technology Project of Henan Province Grant No. 242102241027, the Key Scientific Research Project of Colleges and Universities of Henan Grant No. 242102241027, and the Doctoral Scientific Research Foundation of Henan Polytechnic University Grant No. B2014-022.

References

[1] B. V. Zee, Y. Li, G. J. A. H. Wetzelaer, P. W. M. Blom, Adv. Mater. **34**, 2108887 (2022).
[2] M. Li, D. K. Mangalore, J. Zhao, J. H. Carpenter, H. Yan, H. Ade, H. Yan, K. Müllen, P. W. M. Blom, W. Pisula, D. M. de Leeuw, K. Asadi, Nat. Commun. **9**, 451 (2018).
[3] F. H. Hasenburg, K. H. Lin, B. V. Zee, P. W. M. Blom, D. Andrienko, G. J. A. H. Wetzelaer, APL Materials **11**, 021105 (2023).
[4] N. B. Kotadiya, P. W. M. Blom, G. A. H. Wetzelaer, Phys. Rev. Applied **11**, 024069 (2019).
[5] J. Wu, H. Cha, T. Du, Y. Dong, W. Xu, C. Lin, J. R. Durrant, Adv. Mater. **34**, 2101833 (2022).
[6] S. Naka, H. Okada, H. Onnagawa, Y. Yamaguchi, T. Tsutsui, Synth. Met., **111**, 331 (2000).
[7] K. Vakhshouri, D. R. Kozub, C. Wang, A. Salleo, E. D. Gomez, Phys. Rev. Lett., **108**, 026601 (2012).
[8] N. Felekidis, A. Melianas, M. Kemerink, Org. Electron. **61**, 318 (2018).
[9] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[10] P. M. Borsenberger, L. Pautmeier, H. Bässler, J. Chem. Phys. **94**, 5447 (1991).
[11] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, A. V. Vannikov, Phys. Rev. Lett. **81**, 4472 (1998).
[12] M. Bouhassoune, S. L. M. van Mensfoort, P. A. Bobbert, R. Coehoorn, Org. Electron. **10**, 437 (2009).
[13] S. Baranovskii, I. Zvyagin, H. Cordes, S. Yamasaki, P. Thomas, Phys. Status Solidi B **230**, 281 (2002).
[14] C. Tanase, E. J. Meijer, P. W. M. Blom, D. M. de Leeuw, Phys. Rev. Lett. **91**, 216601 (2003).
[15] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, M. A. J. Michels, Phys. Rev. Lett. **94**, 206601 (2005).
[16] L. H. Luo, L. G. Wang, Y. L. Liang, L. Zhang, Y. J. Wang, Optoelectron. Adv. Mat. **16**(7-8), 373 (2022).
[17] L. G. Wang, C. G. Wang, Y. L. Liang, L. Zhang, J. Y. Liu, J. Optoelectron. Adv. M. **25**(3-4), 158 (2023).
[18] A. V. Nenashev, F. Jansson, J. O. Oelerich, D. Huemmer, A. V. Dvurechenskii, F. Gebhard, S. D. Baranovskii, Phys. Rev. B **87**, 235204 (2013).
[19] A. V. Nenashev, J. O. Oelerich, A. V. Dvurechenskii, F. Gebhard, S. D. Baranovskii, Phys. Rev. B **96**, 035204 (2017).
[20] S. D. Baranovskii, Phys. Status Solidi A **215**, 1700676 (2018).
[21] J. O. Oelerich, D. Huemmer, S. D. Baranovskii, Phys. Rev. Lett. **108**, 226403 (2012).
[22] A. Miller, E. Abrahams, Phys. Rev. **120**, 745 (1960).
[23] R. Coehoorn, P. A. Bobbert, Phys. Stat. Sol. A **209**, 2354 (2012).
[24] B. I. Shklovskii, Sov. Phys. Semicond. **6**, 1964 (1973).
[25] S. Marianer, B. I. Shklovskii, Phys. Rev. B **46**, 13100 (1992).
[26] F. Jansson, S. D. Baranovskii, F. Gebhard, R. Österbacka, Phys. Rev. B **77**, 195211 (2008).
[27] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H. L. Yip, T. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, Y. Zou, Joule **3**, 1140 (2019).
[28] T. Upreti, Y. Wang, H. Zhang, D. Scheunemann, F. Gao, M. Kemerink, Phys. Rev. Applied **12**, 064039 (2019).
[29] F. Gao, Joule **3**, 908 (2019).
[30] J. C. Blakesley, D. Neher, Phys. Rev. B **84**, 075210 (2011).

*Corresponding author: wangliguo@hpu.edu.cn