

Electric field dependence of charge-carrier hopping transport at large carrier concentrations in disordered organic solids: Meyer-Neldel and Gill energies

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Abstract. Effective medium approach has been extended to describe the temperature dependent hopping charge-carrier mobility at arbitrary electric fields in the large carrier density transport regime. We take into account the spatial energy correlations in organic materials with Gaussian disorder. The theory is applied to describe recent experimental measurements of the electron transport properties in a C₆₀-based OFET for different lateral electric fields F_{DS} . Since this model is not limited to zero-field mobility, it allows a more accurate evaluation of important material parameters from experimental data measured at a given electric field. The shift of the Meyer-Neldel energy E_{MN} upon applied lateral electric field F_{DS} and the Gill energy E_G upon the gate voltage V_G in an OFET is shown to be a consequence of the spatial energy correlation effects in the organic semiconductor film. We showed that both the Meyer-Neldel and Gill energies can be used for estimating the width of the Gaussian density-of-states distribution.

1. Introduction

Charge carrier transport in organic materials has been consistently described by a formalism based on hopping in a Gaussian density-of-states (DOS) distribution. The Gaussian Disorder model (GDM) originally suggested by Bässler and co-authors [1], has been developed specifically for the low-carrier-density hopping transport regime. For large carrier concentrations the charge carrier mobility depends also on carrier concentration which has been recently described within an Extended Gaussian Disorder model (EGDM) [2-5]. Despite the success of the disorder formalism in rationalizing many aspects of the charge transport in organic semiconductors, the electrical transport mechanisms in realistic organic electronic devices are still not completely understood. This applies, for instance, to the dependence of the charge carrier mobility on the electric field (F) and, in particular, to the $\ln \mu \propto F^{1/2}$ "Poole-Frenkel" (PF) type dependence being experimentally observed in a rather broad field range. Parris et

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al. [6] and Novikov et al. [7] have suggested on the basis of their computer simulations of the charge transport in the low-carrier-concentration limit with accounting for long-range spatial energy correlations a so-called Correlated Disorder model (CDM). The description of charge transport at high carrier concentrations was addressed just recently using numerical simulations Novikov [8] and Bouhassoune et al. [9] suggested a so-called Extended Correlated Disorder model (ECDM).

In the present study we suggest an analytical Effective medium approach to describe charge mobility in disordered organic solids, which is formulated for arbitrary electric fields at high carrier concentrations and takes into account spatial energy correlations. We applied this theory to analyze recent experimental data on electron mobilities measured in a benchmark OFET device based on C₆₀ semiconductor films. We study the influence of the electric field on the so-called Meyer-Neldel (MN) compensation rule [10] typically observed for the temperature dependence of the charge carrier mobility in a high-carrier-concentration regime. In context of the charge transport in OFETs, the MN rule suggests a empirical relation between the Arrhenius activation energy E_a and the mobility prefactor. As our previous treatment [11] was limited to zero-electric field, we now extended it for arbitrary electric fields to study simultaneously the effect of the carrier concentration and the electric field on the Meyer-Neldel phenomenon for the OFET mobility. The presented theory was also used to describe the recently observed MN-type effect in OFETs regarding $\mu(T)$ dependence upon varying the electric field.

2. Theoretical formulation

Our analytic theoretical treatment is focused on the description of the electric-field dependence of the drift charge-carrier mobility in a random organic system at different temperatures and carrier concentrations, and is based on an Effective Medium approximation (EMA). Let us consider a random 3D hopping transport system with an applied electric field $\mathbf{F} = \{F, 0, 0\}$. In general the effective drift hopping mobility μ_e can be obtained as

$$\mu_e = ak_0 \frac{W_e^+ - W_e^-}{F}, \quad (1)$$

where $W_e^\pm = \langle \tau_{12}^\pm \rangle^{-1}$, $\langle \tau_{12}^\pm \rangle = \int_{-\infty}^{\varepsilon_t} P(\varepsilon) \{W_{12}^\pm(\varepsilon_t, \varepsilon)\}^{-1} d\varepsilon / \int_{-\infty}^{\varepsilon_t} P(\varepsilon) d\varepsilon$.

Coefficient k_0 emerges in Eq. (1) to include the generalized Einstein equation. We use a Miller-Abrahams-type jump rate $W_{12}^\pm(\varepsilon_t, \varepsilon) = W_0 \exp\left\{-\left[|\varepsilon_t - \varepsilon \mp eaF| + (\varepsilon_t - \varepsilon \mp eaF)\right]/2k_B T\right\}$. Here $W_0 = \nu_0 \exp(-2r_t/b)$, where ν_0 is the attempt-to-escape frequency, r_t is the jump distance below the effective transport energy ε_t [12], $a = N^{-1/3}$, N is the site concentration and b is the localization radius of the charged site. Configuration averaging $\langle \dots \rangle$ of the hopping transitions times has to be done over the energy distribution of empty localized states, viz. by using the function $P(\varepsilon) = g(\varepsilon)[1 - f(\varepsilon, \varepsilon_F)]$, where $f(\varepsilon, \varepsilon_F)$ is the Fermi-Dirac distribution. The Fermi energy level ε_F can be determined from the following transcendental equation $n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon, \varepsilon_F)$ for the carrier concentration n . The coefficient k_0 (cf. Eq. (1)) in this case can be determined as $k_0 = 1 - \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f^2(\varepsilon, \varepsilon_F) / \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon, \varepsilon_F)$. In the present study we assume a Gaussian DOS distribution $g(\varepsilon)$ with the width σ as generally accepted to be appropriate for disordered

organic media $g(\varepsilon) = (N/\sigma\sqrt{2\pi})\exp[-(1/2)(\varepsilon/\sigma)^2]$. After combining, we can express the effective charge carrier mobility μ_e as

$$\mu_e = \mu_0 k_0 \left(\frac{r_t}{a}\right)^2 \exp\left(-2\frac{r_t}{b}\right) \frac{(Y_e^+)^{-1} - (Y_e^-)^{-1}}{f}, \quad (2)$$

where

$$Y_e^\pm = \frac{\int_{-\infty}^{x_i} dt \frac{\exp\left\{-\frac{t^2}{2} + \frac{1}{2}[|x_i - t \mp f| + (x_i - t \mp f)x]\right\}}{1 + \exp[-(t - x_F)x]}}{\int_{-\infty}^{x_i} dt \frac{\exp\left\{-\frac{t^2}{2}\right\}}{1 + \exp[-(t - x_F)x]}}. \quad (3)$$

Here $Y_e^\pm = W_e^\pm/W_0$, $f = eaF/\sigma$, $x = \sigma/k_B T$, $x_F = \varepsilon_F/\sigma$, $x_i = \varepsilon_i/\sigma$, $\mu_0 = ea^2\nu_0/\sigma$. The effective transport energy ε_t in our method does not depend on the applied electric field F and hence for a Gaussian DOS distribution can be determined from the following transcendental equation derived for zero-field mobility [3]

$$\frac{1}{\sqrt{2\pi}} \frac{\exp\left(-\frac{1}{2}x_i^2\right)}{1 + \exp[-(x_i - x_F)x]} \left\{ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x_i} dt \frac{\exp\left(-\frac{1}{2}t^2\right)}{1 + \exp[(t - x_F)x]} \right\}^{-\frac{4}{3}} = \frac{3}{2} \left(\frac{4\pi}{3B}\right)^{\frac{1}{3}} x \frac{b}{a}. \quad (4)$$

Here parameter $B = 2.7$ being determined according to percolation criteria [13]. Factor r_t is calculated by

$$r_t = a \left\{ \frac{4\pi}{3B} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x_i} dt \frac{\exp\left(-\frac{1}{2}t^2\right)}{1 + \exp[-(t - x_F)x]} \right\}^{\frac{1}{3}}. \quad (5)$$

The results of our analytical calculation by Eq. (2) are in very good agreement with the computer simulations data by Pasveer et al. [2] obtained within the EGDM approximation for temperature-, field- and carrier-concentration- dependences of the charge carrier mobility in a random (non-correlated) organic system. It is well established that a PF-type field dependence of the charge carrier mobility can be reproduced over an extended interval of electric fields only when some kind of correlated disorder is taken into account in the framework of the Correlated Disorder model (CDM) or the Extended Correlated Disorder model (ECDM).

Hence, hereafter in our theoretical description we will use the concept of energy correlations. Generally, accounting for the energy correlated disorder effects is not amenable to analytical treatment, although it might be solved by computer simulations [8, 9].

We therefore will use here in our analytical treatment some key ingredients from the numerical simulations studies performed before within the CDM and ECDM [7, 8, 9], in particular, (i) the width of the so-called correlated DOS, σ_c , has to be somewhat smaller than the initial non-correlated σ , (ii) the typical jump length, governing the effective charge carrier mobility, depends not only on electric field but also on carrier concentration. Thus, for calculation of the field-, temperature-, and carrier-concentration- dependences of the charge carrier mobility in disordered organic semiconductors we will hereafter use Eq. (2-5) obtained within EGDM approximation with accounting for energy correlation effects by substituting the parameters σ , f by σ_c , $f_c y$, respectively, where $\sigma_c = 0.83\sigma$, $y = (1 - n/N)^m$, $m = -9.69 + 10.81(\sigma/k_B T) - 0.905(\sigma/k_B T)^2$, $f_c = h_c \sqrt{x_c/2}$, $h_c = \sqrt{eaF/\sigma_c}$, $x_c = \sigma_c/k_B T$.

3. Effect of electric field and carrier concentration on “Meyer-Neldel” and “Gill” energies

We discriminate between the isokinetic temperatures resulting from intersection of $\ln(\mu) \propto T^{-1}$ upon varying carrier concentration and that upon varying applied electric field and call them Meyer-Neldel- and Gill- temperature, respectively. According to the results, the Meyer-Neldel temperature (denoted as T_1) and Gill temperature (denoted as T_2) are not constant but depend on the electric field F and relative carrier concentration n/N , respectively. This effect indeed can be well reproduced within the present EMA model. The field dependence of T_1 can be parameterized as follows

$$\frac{k_B T_1}{\sigma} = 0.5 + 0.029 \frac{eaqF}{\sigma} - 0.039 \left(\frac{eaqF}{\sigma} \right)^2. \quad (6)$$

Here q is a parameter to be described below.

In line to that, the Gill-temperature T_2 tends to decrease with increasing carrier concentration n/N . This carrier density dependence of T_2 can be well approximated by

$$\frac{k_B T_2}{\sigma} = 0.416 - 0.037 \log_{10} \left(\frac{n}{N} \right) - 0.0031 \left[\log_{10} \left(\frac{n}{N} \right) \right]^2. \quad (7)$$

From our analyze we conclude that the change of the MN-temperature T_1 upon applied electric field and the decrease of the Gill-temperature T_2 with increasing n/N results from the presence of energy correlation effects, namely, due to the decrease of the typical jump length with increasing carrier concentration. It should be pointed out that the above calculated dependences for T_1 and T_2 are only relevant to the range of electric fields where the PF-type field dependence holds.

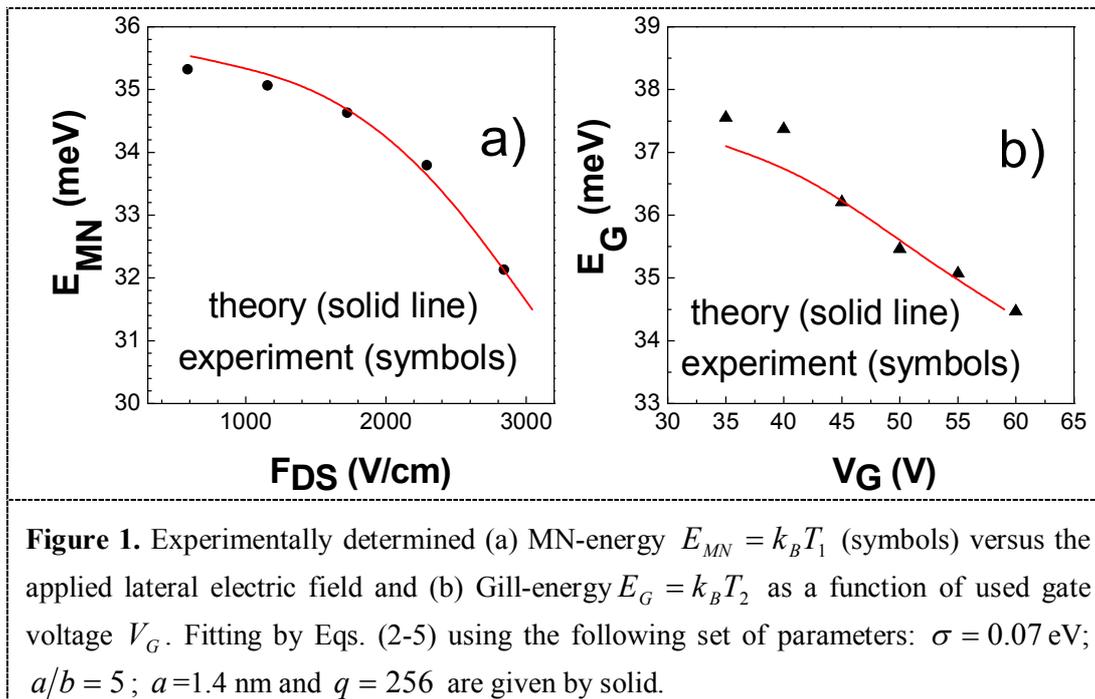
The results of the above calculated charge carrier mobility in the high-carrier-concentration limit can be used to estimate the energetic disorder parameter σ from experimental data basically by two different methods: First, the experimentally measured MN-temperature T_1 ($E_{MN} = k_B T_1$) at a given electric field F (within the field interval where a PF-type dependence is obeyed) is inserted into Eq. (6). It results in a quadratic equation to calculate the parameter σ . The solution reads

$$\sigma = E_{MN} A \left(1 + \sqrt{1 + \left(\frac{eaqF}{E_{MN}} \right)^2 \frac{0.078}{A^2}} \right), \quad A = 1 - 0.029 \frac{eaqF}{E_{MN}}. \quad (8)$$

The experimentally measured Gill-temperature T_2 ($E_G = k_B T_2$) at a given high carrier concentration n/N (being determined by a gate voltage (V_G) in an OFET) is substituted into Eq. (7), and yields the following relation for calculating σ .

$$\sigma = \frac{E_G}{0.416 - 0.037 \log_{10} \left(\frac{n}{N} \right) - 0.0031 \left[\log_{10} \left(\frac{n}{N} \right) \right]^2}. \quad (9)$$

To use Eq. (9) one has, however, to know the effective carrier concentration in a thin conductive channel of an OFET, which demonstrates a highly non-uniform distribution - strongly decreasing from the semiconductor/insulator interface into the bulk. Thus, the first of the above-mentioned methods seems to be more appropriate for estimating the disorder parameter σ from experimental data. A big advantage of the present theoretical model is that it does not require an extrapolation of experimental data to zero electric field.



For quantitative description of the lateral-field dependence of the OFET mobility one has to involve a concept of a strong inhomogeneity of the lateral electric field inside the accumulation layer formed in an OFET caused by an inhomogeneous morphology of the semiconductor, which results in strong local fields confined to specific places establishing major energetic barriers and, hence, controlling the overall (effective) hopping charge mobility through the OFET channel, as suggested elsewhere [14]. Thus, it is actually the effective local field that should be used in Eqs. (6, 8) instead of the average

applied electric field. The ratio q between the local electric field strength and that averaged over the transistor channel V_d/L can be determined from the field dependence of E_{MN} .

In fact, a set of just two E_{MN} values measured at two different electric fields inserted into Eq. (8) enables calculating σ and q parameters. The effects observed in Figure 1(a) and (b) can only be described provided that energy correlation effects are taken into account. This suggests an important experimental test for the presence of energy correlations in an organic semiconductor.

4. Conclusion

An analytical EMA theory was formulated to describe the effect of electric field on the charge carrier mobility at high carrier concentrations in disordered organic semiconductors at large carrier concentrations with accounting for energy correlation effects. The EMA theory predicts that the Meyer-Neldel temperature (T_1) and Gill temperature (T_2) are not constant but depend on the electric field and carrier concentration, respectively; and this found to be a consequence of spatial energy correlations in organic disordered materials. We show that both above temperatures can be used for estimating the energy disorder parameter – the width of the DOS distribution. The present model allows more accurate evaluation of important material parameters from experimental data measured at arbitrary electric field without extrapolation of experimental data to the zero-electric field.

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