IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

# Weak-field carrier hopping in disordered organic semiconductors: the effects of deep traps and partly filled density-of-states distribution

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 9899

(http://iopscience.iop.org/0953-8984/14/42/305)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.96
The article was downloaded on 18/05/2010 at 15:13

Please note that terms and conditions apply.

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 9899–9911 PII: S0953-8984(02)34455-2

# Weak-field carrier hopping in disordered organic semiconductors: the effects of deep traps and partly filled density-of-states distribution

**V I Arkhipov[1], P Heremans[1], E V Emelianova[2,4], G J Adriaenssens[2] and H Bässler[3]**

[1] IMEC, Kapeldreef 75, B-3001 Heverlee-Leuven, Belgium
[2] Laboratorium voor Halfgeleiderfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium
[3] Institut für Physikalische-, Kern- und Makromolekulare Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

Received 1 March 2002
Published 11 October 2002
Online at stacks.iop.org/JPhysCM/14/9899

**Abstract**
An analytic model of the weak-field carrier transport in an energetically disordered and positionally random hopping system is formulated. Within the framework of this model, the carrier mobility can be calculated by either direct averaging of carrier hopping rates or by the use of the effective transport energy concept. It is shown that multiple carrier jumps within pairs of occasionally close hopping sites affect the position of the effective transport level on the energy scale. In good quantitative agreement with experimental data and results of Monte Carlo simulation, the temperature and concentration dependences of the mobility can be almost perfectly factorized, i.e. represented as a product of two functions one of which depends solely upon the temperature while the other governs the dependence upon the density of localized states. The model is also used for the calculation of trap-controlled hopping mobility and for the analysis of hopping transport at high charge-carrier densities.

## 1. Introduction

Charge-carrier hopping within a positionally random and energetically disordered system of localized states is commonly accepted as an adequate model for describing conductivity in disordered organic semiconductors [1,2]. The occurrence of the positional disorder will almost inevitably give rise to energy disorder via the dependence of the potential energy of interaction upon the distance between interacting particles [3,4]. Most hopping models are based on the Miller–Abrahams [5] expression for the rate of carrier jumps, $\nu(r, E_s, E_t)$, over the distance $r$

[4] Author to whom any correspondence should be addressed.

between a starting state of the energy $E_s$ and the target site of the energy $E_t$. This expression can be written as

$$\nu(r, E_s, E_t) = \nu_0 \exp[-u(r, E_s, E_t)], \qquad u(r, E_s, E_t) = 2\gamma r + \frac{\eta(E_t - E_s)}{kT}, \tag{1}$$

where $u$ is the hopping parameter, $\nu_0$ the attempt-to-jump frequency, $\gamma$ the inverse localization radius, $T$ the temperature, $k$ the Boltzmann constant, and $\eta$ the unity step function. Although the distance and the energy difference between the starting and target sites affect the jump rate almost identically there is one important difference that gives rise to very different $r$- and $E$-hopping modes.

The distance-dependent factor in equation (1) is completely symmetric, i.e. the distance between hopping sites affects the rates of backward and forward jumps similarly. A site which is remote from all its neighbours in a positionally random system of monoenergetic hopping sites cannot be considered as a trap for carriers because the trapping time will be exactly equal to the release time. It is equally difficult for a carrier to be released and to be trapped by such an isolated localized state. However, this is not the case for an energetically random system. While energetically upward jumps require thermal activation, downward jumps imply dissipation of the excess energy via phonon emission. The former takes a much longer time than the latter and, therefore, the rates of backward and forward jumps between two fixed states of different energies can be very different. Consequently, a deep localized state can promptly capture a carrier and keep it localized over a long time. This asymmetry makes the energy disorder much more important as far as charge transport characteristics are concerned.

Nonetheless, the interplay between jump distance and the energy difference between starting and target sites plays an important role in hopping transport and one cannot disregard the positional disorder. In general, the probability that the jump will be made to some site of the specific energy $E_t$ depends upon the temperature, $T$, the density-of-states (DOS) distribution, $g(E)$, the localization radius $(1/\gamma)$, *and* the energy of the starting site, $E_s$. However, for a sufficiently steep DOS function the most probable value of the energy $E_t$ does not depend upon $E_s$ if the starting site is sufficiently deep [6, 7]. In other words, practically all carriers localized in a deep tail of the DOS distribution will eventually jump to one of the shallower states whose energies are close to some universal value which is traditionally referred to as the transport energy, $E_{tr}$ . Amongst several methods suggested over the last decades [8–10], that based on the concept of effective transport energy proved to be especially efficient for calculation of carrier mobility in disordered materials [11, 12]. The use of this concept considerably simplifies the problem and essentially reduces it to that of trap-controlled transport with a broad energy distribution of localized states [13].

Both analytic models and Monte Carlo simulations of hopping transport in disordered organic materials are normally restricted to the random walk of a single carrier [2] within a Gaussian DOS distribution. However,

(i) organic semiconductors and conjugated polymers often have 'traps' in addition to a Gaussian DOS of 'transport sites'; and
(ii) electronic applications of these materials require high densities of the injection current and/or high doping levels.

Since the carrier density in a doped polymer can be comparable with the density of localized states in the deep tail of the DOS distribution, those states can be fully filled by carriers. Both deep traps and filling of localized states can strongly affect the field and temperature dependences of the hopping conductivity. In the present paper we use the concept of the effective transport energy in order to formulate an analytic model describing the effects of

traps and high carrier densities on the equilibrium weak-field carrier hopping in disordered organic materials.

## 2. Average hopping parameter

Carrier jumps from a fixed starting site to a target site can be characterized by hopping parameter $u$ defined by equation (1). In a positionally random system of localized states, the average number of target sites for a starting site of energy $E_s$, $n(E_s, u)$, whose hopping parameters are not larger than $u$ can be calculated as

$$n(E_s, u) = 4\pi \int_0^{u/2\gamma} \mathrm{d}r\, r^2 \int_{-\infty}^{E_s+kT(u-2\gamma r)} \mathrm{d}E_t\, g(E_t)$$
$$= \frac{4\pi}{3}\left(\frac{u}{2\gamma}\right)^3 \left[\int_{-\infty}^{E_s} \mathrm{d}E_t\, g(E_t) + \int_{E_s}^{E_s+kTu} \mathrm{d}E_t\, g(E_t)\left(1 - \frac{E_t - E_s}{kTu}\right)^3\right]. \tag{2}$$

The first term in the right-hand side of equation (2) gives the number of target states that are deeper than the starting site and the second one describes the number of shallower states. The probability density, $w(E_s, u)$, of finding a nearest hopping neighbour of the hopping parameter $u$ is determined by the Poisson distribution as

$$w(E_s, u) = \exp[-n(E_s, u)]\frac{\partial n(E_s, u)}{\partial u}. \tag{3}$$

Equation (3) forms a basis for calculating the average hopping parameter, $\langle u\rangle(E_s)$, for carrier jumps from a starting site of energy $E_s$. Using equation (3) as a distribution function for averaging the hopping parameter yields

$$\langle u\rangle(E_s) = \int_0^\infty \mathrm{d}u\, u \exp[-n(E_s, u)]\frac{\partial n(E_s, u)}{\partial u} = \int_0^\infty \mathrm{d}u \exp[-n(E_s, u)]. \tag{4}$$

The average squared jump distance, $\langle r^2\rangle(E_s)$, can be evaluated as

$$\langle r^2\rangle(E_s) = \frac{3}{5}\left(\frac{\langle u\rangle}{2\gamma}\right)^2 \left[\int_{-\infty}^{E_s} \mathrm{d}E_t\, g(E_t) + \int_{E_s}^{E_s+kTu} \mathrm{d}E_t\, g(E_t)\left(1 - \frac{E_t - E_s}{kTu}\right)^5\right]$$
$$\times \left[\int_{-\infty}^{E_s} \mathrm{d}E_t\, g(E_t) + \int_{E_s}^{E_s+kTu} \mathrm{d}E_t\, g(E_t)\left(1 - \frac{E_t - E_s}{kTu}\right)^3\right]^{-1}. \tag{5}$$

On average, every carrier jump increases the packet spreading, and the relative contribution, $D_s$, of carriers jumping from starting sites of energy $E_s$ to the equilibrium hopping diffusivity, $D$, can be evaluated as

$$D_s = \nu_0 \exp[-\langle u\rangle(E_s)]\langle r^2\rangle(E_s). \tag{6}$$

Averaging hopping rates over $E_s$ and using the Einstein relation yields the following expression for the equilibrium mobility $\mu$:

$$\mu = \frac{e\nu_0}{kT}\int_{-\infty}^{\infty} \mathrm{d}E_s \exp[-\langle u\rangle(E_s)]\langle r^2\rangle(E_s) f(E_s), \tag{7}$$

where $f(E)$ is the normalized energy distribution function of localized carriers.

The time-of-flight (TOF) technique is commonly used for the experimental study of charge-carrier mobility in both organic and inorganic non-crystalline materials. TOF measurements imply a low carrier density that allows neglect of the possibility of trap filling.

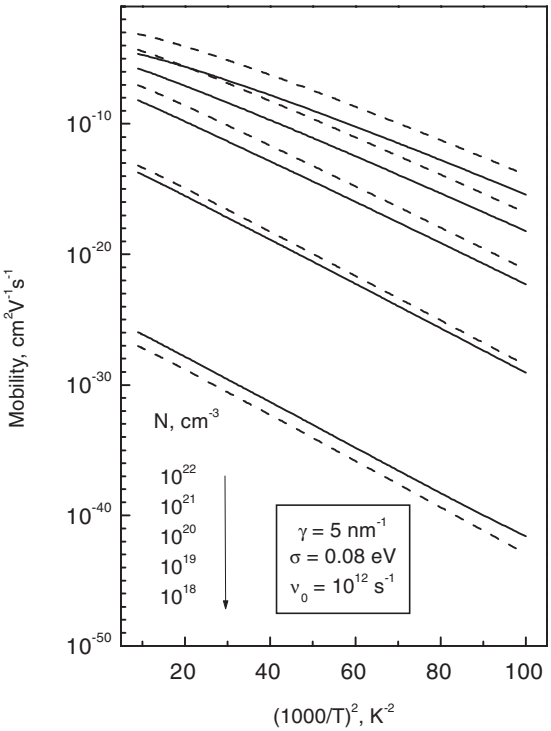


**Figure 1.** Temperature dependence of the equilibrium drift mobility in a disordered hopping system with a Gaussian DOS distribution of localized states. Solid and dashed lines are calculated from equations (9) and (19), respectively.

Under these conditions one can use a single-carrier distribution function. The equilibrium TOF mobility can, therefore, be calculated by the use of the Boltzmann distribution:

$$f(E) = \left[\int_{-\infty}^{\infty} \mathrm{d}E\, g(E) \exp\left(-\frac{E}{kT}\right)\right]^{-1} g(E) \exp\left(-\frac{E}{kT}\right). \tag{8}$$

Substituting this distribution function into equation (7) yields

$$\mu = \frac{e\nu_0}{kT}\left[\int_{-\infty}^{\infty} \mathrm{d}E_s\, g(E_s) \exp\left(-\frac{E_s}{kT}\right)\right]^{-1} \times \int_{-\infty}^{\infty} \mathrm{d}E_s \exp[-\langle u\rangle(E_s)]\langle r^2\rangle(E_s) g(E_s) \exp\left(-\frac{E_s}{kT}\right). \tag{9}$$

The temperature dependence of the mobility, calculated from equation (9) for a Gaussian DOS distribution of width $\sigma$,

$$g(E) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left(-\frac{E^2}{2\sigma^2}\right), \tag{10}$$

is shown in figure 1 for different values of the total density of localized states, $N$. All the curves are almost perfect straight lines if plotted as $\log \mu$ versus $1/T^2$. Although absolute values of the mobility strongly depend upon $N$, the slope increases by $<15\%$ when the density of hopping sites decreases by four orders of magnitude. This indicates that the equilibrium mobility can be fairly well represented in a factorized form as

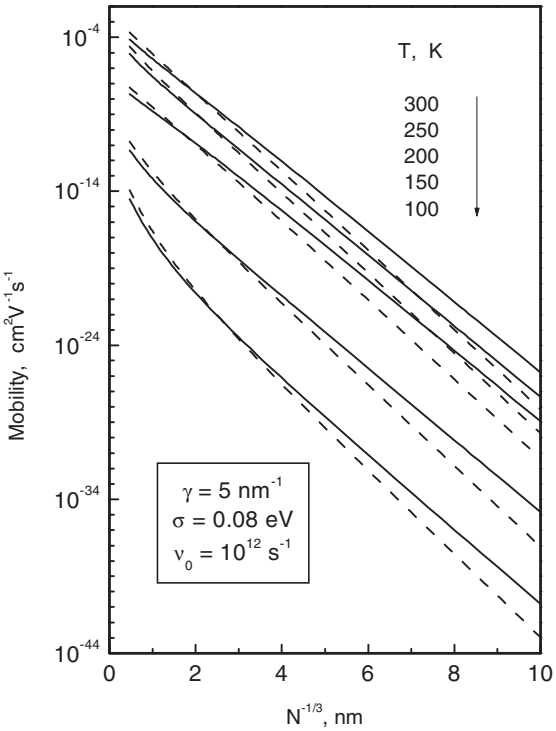


**Figure 2.** Concentration dependence of the equilibrium drift mobility in a disordered hopping system with a Gaussian DOS distribution of localized states. Solid and dashed curves are calculated from equations (9) and (19), respectively.

$$\mu = \mu_0 \varphi(N) \exp\left[-\left(\frac{c\sigma}{kT}\right)^2\right], \tag{11}$$

with the numeric parameter $c$ changing from 0.59 at $N = 10^{22}\ \mathrm{cm}^{-3}$ to 0.68 at $N = 10^{18}\ \mathrm{cm}^{-3}$. Both the form of equation (11) and the value of $c$ are in good quantitative agreement with the results of Monte Carlo simulations ($c = 0.67$) and predictions of the effective medium model ($c = 0.64$).

The concentration dependence of the equilibrium mobility is illustrated in figure 2, parametric in the temperature. The curves plotted in this figure imply an exponential dependence of the mobility upon the density of hopping sites,

$$\varphi(N) = \exp\left(-\frac{b\gamma}{N^{1/3}}\right), \tag{12}$$

with the numeric parameter $b$ being almost independent of the temperature. The model, based on the averaging carrier jump rates, is thus capable of describing both the temperature and concentration dependences of the equilibrium carrier mobility in a random hopping system with a Gaussian DOS distribution. It is worth noting that deviations of the curves plotted in figures 1 and 2 from the dependences described by equations (11) and (12) mainly occur at high temperatures and concentrations of localized states. These deviations are probably due to the fact that carrier jumps to next-nearest hopping neighbours, which are quite feasible at high $T$ and $N$ [2], are disregarded for the present considerations.

## 3. Effective transport energy

The average number of hopping neighbours given by equation (2) accounts for both downward and upward jumps in energy. However, under thermal equilibrium conditions practically all carriers are localized in relatively deep hopping sites. Therefore, for most carriers the nearest vacant hopping neighbours have energies that are higher than the energies of the sites that the carriers currently occupy. This fact implies a much higher probability of upward jumps than of downward jumps, which in turn allows neglecting the first term in the right-hand side of equation (2). The result reads

$$n(E_s, u) = \frac{\pi}{6\gamma^3}\int_{E_s}^{E_s+kTu} \mathrm{d}E_t\, g(E_t)\left(u - \frac{E_t - E_s}{kT}\right)^3. \tag{13}$$

One can consider the average number of hopping neighbours as a function of the energy $E_{tr}$ defined as

$$E_{tr} = E_s + kTu, \tag{14}$$

rather than of the hopping parameter $u$. Carrying out this replacement of variables in equation (13) yields the average number of hopping neighbours of energies not larger than $E_{tr}$ for a starting site of energy $E_s$:

$$n(E_s, E_{tr}) = \frac{\pi}{6}(\gamma kT)^{-3}\int_{E_s}^{E_{tr}} \mathrm{d}E_t\, g(E_t)(E_{tr} - E_t)^3. \tag{15}$$

An upward carrier jump from a starting site is possible if there is at least one such hopping neighbour, i.e. from $n(E_s, E_{tr}) = 1$ on. The use of this condition in equation (15) leads to the following transcendental equation for the energy $E_{tr}$:

$$\int_{E_s}^{E_{tr}} \mathrm{d}E_t\, g(E_t)(E_{tr} - E_t)^3 = \frac{6}{\pi}(\gamma kT)^3. \tag{16}$$

If the DOS distribution decreases with energy faster than $|E|^{-4}$ then (i) the value of the integral in the left-hand side of equation (16) depends only weakly upon the lower bound of integration for sufficiently deep starting sites and (ii) a major contribution to the integral comes from states with energies around $E_{tr}$. Physically, this means that target sites for thermally assisted upward carrier jumps are located around the energy $E_{tr}$ independent of the energy of starting sites and, therefore, equation (16) can be reduced to

$$\int_{-\infty}^{E_{tr}} \mathrm{d}E_t\, g(E_t)(E_{tr} - E_t)^3 = \frac{6}{\pi}(\gamma kT)^3. \tag{17}$$

Averaging rates of carrier jumps to the effective transport level, estimating the average squared jump distance as

$$\langle r^2\rangle = \left[\int_{-\infty}^{E_{tr}} \mathrm{d}E\, g(E)\right]^{-2/3},$$

and using the Einstein relation yields the following expression for the equilibrium mobility:

$$\mu = \frac{e\nu_0}{kT}\left[\int_{-\infty}^{E_{tr}} \mathrm{d}E\, g(E)\right]^{-2/3}\int_{-\infty}^{E_{tr}} \mathrm{d}E_s\, f(E_s)\exp\left(-\frac{E_{tr} - E_s}{kT}\right). \tag{18}$$

For the equilibrium single-particle distribution function given by equation (8) this expression yields

$$\mu = \frac{e\nu_0}{kT}\left[\int_{-\infty}^{\infty} \mathrm{d}E\, g(E)\exp\left(-\frac{E}{kT}\right)\right]^{-1}\left[\int_{-\infty}^{E_{tr}} \mathrm{d}E\, g(E)\right]^{1/3}\exp\left(-\frac{E_{tr}}{kT}\right). \tag{19}$$

The temperature and concentration dependences of the mobility calculated from equation (9) are plotted as dashed curves in figures 1 and 2, respectively. The slopes of all the curves in figure 1 are extremely similar while there are small differences in slopes in figure 2. These differences are probably caused by different estimates for the typical jump distances in equations (9) and (19). In general, the transport energy approximation effectively reduces consideration of carrier hopping in a disordered system to the multiple-trapping problem.

## 4. The role of backward carrier jumps

The approach outlined in the previous section disregards repeated carrier jumps between two accidentally close hopping neighbours both of which are isolated from other localized states. Although such jumps are important as far as ac conductivity is concerned, they do not contribute to the dc current and, concomitantly, to the equilibrium carrier mobility. Therefore, although equation (17) does determine the energy level of most probable upward jumps, the energy $E_{tr}$ is not necessarily the genuine transport energy. In order to calculate the latter, one must account for the backward jumps. Now we embark on this calculation.

After an upward jump over the distance $r$, a carrier will, most probably, not return to the starting site if there is another hopping neighbour of the target site with a hopping parameter that is smaller than $2\gamma r$ *outside* the sphere of radius $r$ centred at the starting site. The average number of such neighbours, $n_b(E_t, r)$, increases with increasing $E_t$ or $r$ as

$$\begin{aligned} n_b(E_t, r) &= 2\pi \int_0^r \mathrm{d}\xi\, \xi^2 \int_{\arccos(\xi/2r)}^{\pi} \mathrm{d}\vartheta\, \sin\vartheta \int_{-\infty}^{E_t+2\gamma kT(r-\xi)} \mathrm{d}E'\, g(E') \\ &= \frac{\pi r^3}{12}\left\{ 11 \int_{-\infty}^{E_t} \mathrm{d}E'\, g(E') + \int_{E_t}^{E_t+2kT\gamma r} \mathrm{d}E'\, g(E') \right. \\ &\quad \left. \times \left[ 8\left(1 - \frac{E'-E_t}{2kT\gamma r}\right)^3 + 3\left(1 - \frac{E'-E_t}{2kT\gamma r}\right)^4 \right] \right\}. \end{aligned} \tag{20}$$

The probability, $w(E_t, r)$, that the target site of the energy $E_t$ has at least one hopping neighbour of hopping parameter smaller than $2\gamma r$ is determined by the Poisson distribution:

$$w(E_t, r) = 1 - \exp[-n_b(E_t, r)]. \tag{21}$$

Since the round-trip carrier jumps do not contribute to transport and relaxation, only those hopping neighbours should be accounted for from which carrier jumps back to initially occupied starting sites are improbable. For upward jumps this condition leads to

$$\begin{aligned} n(E_s, u) &= 4\pi \int_0^{u/2\gamma} \mathrm{d}r\, r^2 \int_{E_s}^{E_s+kT(u-2\gamma r)} \mathrm{d}E_t\, g(E_t)\{1 - \exp[-n_b(E_t, r)]\} \\ &= 4\pi \int_{E_s}^{E_s+kTu} \mathrm{d}E_t\, g(E_t) \int_0^{(1/2\gamma)[u-(E_t-E_s)/kT]} \mathrm{d}r\, r^2\{1 - \exp[-n_b(E_t, r)]\}. \end{aligned} \tag{22}$$

Carrying out again the replacement of variables described by equation (14), and using the condition $n(E_s, E_{tr}) = 1$, yields the transcendental equation for the effective transport energy which accounts for the possibility of backward carrier jumps:

$$4\pi \int_{-\infty}^{E_{tr}} \mathrm{d}E_t\, g(E_t) \int_0^{(E_{tr}-E_t)/2\gamma kT} \mathrm{d}r\, r^2\{1 - \exp[-n_b(E_t, r)]\} = 1. \tag{23}$$

Equations (20) and (23) thus determine the genuine transport energy which precludes return of carriers into initially occupied states and, in a sense, is fully equivalent to the mobility edge in multiple-trapping models.

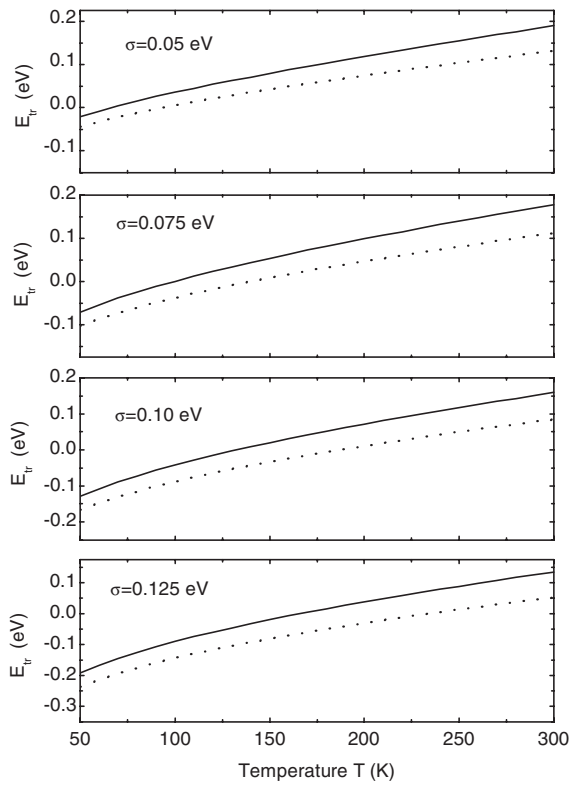


**Figure 3.** Temperature dependence of the effective transport energy in a disordered hopping system with a Gaussian DOS distribution. The data shown by the solid and dashed curves are calculated from equations (23) and (17), respectively, for $\gamma = 10\ \mathrm{nm}^{-1}$, and $N = 10^{22}\ \mathrm{cm}^{-3}$.

The effect of backward carrier jumps on the temperature dependence of the effective transport energy is illustrated by solid curves in figure 3 for a random hopping system with Gaussian DOS distributions of different widths $\sigma$. Dashed curves in this figure show the temperature dependences of the effective transport energy calculated from equation (17) without accounting for backward jumps. A common feature of these results is that, at some temperature, every curve crosses the zero energy level at which the DOS has a maximum. At first glance this seems to be an artefact because, even at high temperatures, most carriers would not jump to states above the maximum of the DOS distribution. In order to resolve this puzzle one may consider the asymptotic behaviour of $E_{tr}$ at higher temperatures and/or low concentration of localized states. The latter condition corresponds to the diluted hopping systems. Solving equation (17) at $T \to \infty$ and/or $N \to 0$ yields

$$E_{tr} = kT\left(\frac{6\gamma^3}{\pi N}\right)^{1/3}. \tag{24}$$

This result is still puzzling: the energy of the effective transport level increases linearly with temperature *above* the maximum of the DOS distribution. However, substituting this formula into equation (14) for the hopping parameter,

$$u = \left(\frac{6\gamma^3}{\pi N}\right)^{1/3} - \frac{E_s}{kT}, \tag{25}$$

clarifies the situation. Equation (25) shows that most carriers jump to states around $E = 0$ through barriers whose thickness is around $(4\pi N/3)^{-1/3}$ and that the energy $E_{tr}$ can be interpreted as a genuine transport energy only while this energy is still below the DOS maximum. The same notion is relevant to the transport energy defined by equation (23). Evaluating the high-temperature asymptote of $E_{tr}$ from equations (20) and (23) yields

$$E_{tr} = \left(\frac{32}{11}\right)^{1/6} kT\left(\frac{6\gamma^3}{\pi N}\right)^{1/3} \cong 1.2kT\left(\frac{6\gamma^3}{\pi N}\right)^{1/3}, \tag{26}$$

indicating that the backward carrier jumps cause the genuine transport energy to be 20% higher than that calculated disregarding the possibility of backward jumps. Substituting the high-temperature/low-concentration expression for $E_{tr}$ from equation (26) into (19) yields

$$\mu_{eq} = \frac{e\nu_0}{kTN^{2/3}} \exp\left[-1.2\left(\frac{6\gamma^3}{\pi N}\right)^{1/3}\right] \exp\left[-\frac{\sigma^2}{2(kT)^2}\right]. \tag{27}$$

Equation (27) proves again that the temperature and concentration dependences of the mobility are factorized at high temperatures and/or in diluted hopping systems. This result also suggests that these dependences will be almost factorized at lower temperatures and in systems with higher concentrations of hopping sites as well. The algebraic $(1/T)$ factor in equation (27) will also affect the $\mu_{eq} \propto \exp[-\sigma^2/2(kT)^2]$ temperature dependence of the mobility; this can be part of the reason for the difference between the numeric factor of 1/2 in equation (27) and the 4/9 obtained in Monte Carlo simulations [2].

## 5. Equilibrium hopping mobility in a system of partially filled localized states

Electronic applications of organic semiconductors imply high densities of the injection current and/or high doping levels in these materials. Realistic operating brightness for organic light emitting diodes (OLEDs) in active matrix colour displays has a peak of some 500–1000 cd m$^{-2}$. In monochrome passive matrix displays, the peak brightness can be several 1000 cd m$^{-2}$. For yellow-orange displays, an efficiency of 10 cd A$^{-1}$ is typical, although not at the highest brightness. The maximum current density in monochrome passive matrix displays is therefore of the order of several 10 to about 100 mA cm$^{-2}$. For active matrix colour displays, the largest current densities will be found for blue, due to the poor eye sensitivity, and are of the order of 100 mA cm$^{-2}$. Further assuming a mobility of the order of $10^{-7}$–$10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$, a layer thickness of 100 nm, and a voltage drop over the organic material, not including the contacts, of 5–10 V depending on the colour, and a current density of several 10 to about 100 mA cm$^{-2}$, the maximum carrier density in OLEDs can be as high as $10^{17}$ to a few $10^{18}$ cm$^{-3}$.

For organic thin-film transistors, typical mobilities are much higher. For polymers, reported mobilities range between a few $10^{-3}$ and a few $10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$, while for polycrystalline materials like pentacene they range from a few $10^{-1}$ to a few cm$^2$ V$^{-1}$ s$^{-1}$. The typical surface carrier density accumulated under the gate insulator is of the order of $10^{12}$–$10^{13}$ cm$^{-2}$. The accumulated charge is localized in a sheet not thicker than a few nanometres. The carrier density in that sheet turns out to be $10^{18}$–$10^{19}$ cm$^{-3}$.

Since the carrier density in a doped polymer can be comparable with the density of localized states, hopping sites in the deep tail of the DOS distribution can be fully filled by carriers. The filling affects energy distributions of both localized carriers and vacant hopping sites. Therefore, the field and temperature dependences of the conductivity must be sensitive to the

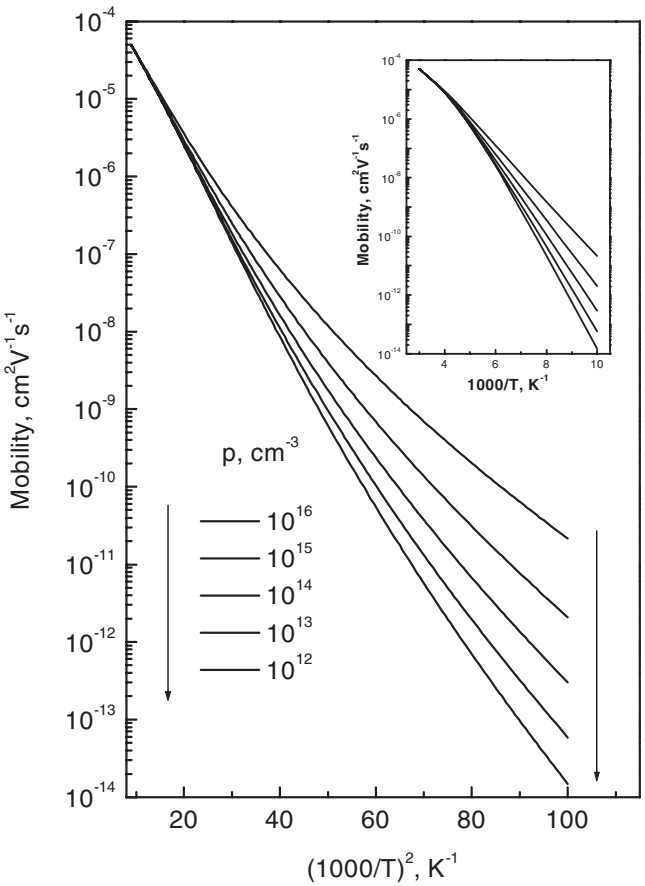


**Figure 4.** Temperature dependence of the equilibrium mobility in a disordered hopping system with a Gaussian DOS distribution parametric in the carrier density for the following set of material parameters: $\gamma = 5$ nm$^{-1}$, $N = 10^{21}$ cm$^{-3}$, $\sigma = 0.08$ eV, $\nu_0 = 10^{12}$ s$^{-1}$. The inset shows the Arrhenius plot for the same set of data.

density of charge carriers. The thermal equilibrium energy distribution of localized carriers is given by a product of the Fermi–Dirac function and the DOS distribution as

$$f(E) = \frac{g(E)}{1+\exp[(E-E_F)/kT]}\left\{\int_{-\infty}^{\infty}\frac{\mathrm{d}E\, g(E)}{1+\exp[(E-E_F)/kT]}\right\}^{-1}. \tag{28}$$

The Fermi energy $E_F$ is determined by the total carrier density $p$ via the following transcendental equation:

$$p = \int_{-\infty}^{\infty}\frac{\mathrm{d}E\, g(E)}{1+\exp[(E-E_F)/kT]}. \tag{29}$$

Concomitantly, the density of vacant hopping sites, $g_v(E)$, should be equal to the difference of the DOS function and the density of occupied sites:

$$g_v(E) = g(E) - pf(E) = \frac{g(E)}{1+\exp[-(E-E_F)/kT]}. \tag{30}$$

Well above the Fermi level, i.e. for $E - E_F \gg kT$, the density of vacant hopping sites is practically equal to the total DOS. Therefore, if the effective transport energy, obtained while

taking the filling of localized states into account, satisfies the condition $E_{tr} - E_F \gg kT$, the mobility can still be calculated from equation (18) with the carrier distribution function given by equation (28). The temperature dependence of the mobility calculated for a Gaussian DOS distribution is shown in figure 4, parametric in the carrier density $p$. At higher temperatures, the conductivity is due to jumps of carriers localized above the Fermi level and, concomitantly, the mobility weakly depends upon the carrier density. At lower temperatures, carrier hopping from the Fermi level takes over and the mobility reveals an Arrhenius-like behaviour with the activation energy decreasing with increasing carrier density as shown in the inset to figure 4.

As mentioned above, the concept of the effective transport energy is applicable if the effective transport level is located well above the Fermi level. However, this condition may not be fulfilled if the temperature is low and/or the carrier density is high. Under such conditions, the effect of filling requires the use of a more sophisticated model based on the averaging of the hopping parameter. This model was described in section 2 of the present paper. In particular, the carrier mobility can be calculated from equations (2), (4), (5), and (7) in which the function $g(E)$ is replaced by $g_v(E)$ and the carrier distribution function is given by equation (28).

## 6. The effect of deep traps on the equilibrium hopping mobility

In addition to the intrinsic DOS distribution, disordered organic semiconductors often have deeper localized states originating from impurities, or from chemical and structural defects. Those states are normally located well below the intrinsic DOS distribution and, therefore, they are often referred to as deep traps. Since the total density of traps is much smaller than the density of intrinsic hopping sites, they cannot noticeably change the effective transport energy. However, these traps can strongly affect charge transport characteristics because, under equilibrium conditions, most carriers will occupy those deep states. In order to calculate the trap-controlled variable-range hopping mobility, one may then use either the method based on averaging hopping parameter or the effective transport energy concept with the DOS distribution that incorporates both intrinsic DOS and distribution of deep traps:

$$g(E) = \frac{N_i}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{E^2}{2\sigma_i^2}\right) + \frac{N_t}{\sqrt{2\pi}\sigma_t} \exp\left[-\frac{(E-E_t)^2}{2\sigma_t^2}\right], \tag{31}$$

where $N_i$ and $N_t$ are the total densities of intrinsic sites and traps, respectively, $\sigma_i$ and $\sigma_t$ the Gaussian variations of the intrinsic site and trap distributions, respectively, and $E_t$ is the energy of the trap DOS maximum.

Temperature dependences of the equilibrium trap-controlled TOF mobility are illustrated in figure 5 for different trap concentrations. At higher temperatures, practically all carriers occupy intrinsic sites and the occurrence of traps does not change the linear log $\mu$ versus $1/T^2$ dependence that is typical for trap-free disordered organic materials. At lower temperatures, the carrier distribution is pinned at the trap peak. Although the effective transport energy is less sensitive to changing temperature than the equilibrium carrier distribution, it is also affected by the traps, especially at high trap densities, as one can see from the inset to figure 5. In fact, traps can serve as an effective hopping transport band at low $T$ and high $N_t$. Pinning the carrier distribution at an almost fixed energy such as $E_t$ and steeper temperature dependence of the effective transport energy lead to a weaker $T$-dependence of $\mu$ at lower temperatures. It is worth noting that the effect of deep traps on the equilibrium carrier mobility is qualitatively similar to that caused by a high carrier density—cf figures 4 and 5.

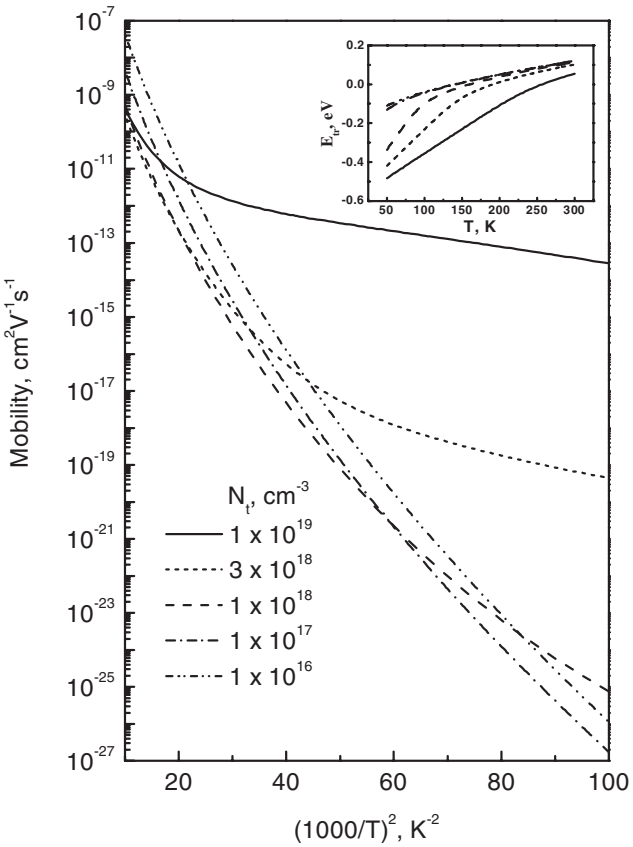


**Figure 5.** The effect of deep traps on the temperature dependence of the equilibrium mobility in a disordered hopping system with a Gaussian DOS distribution. The inset illustrates the temperature dependence of the effective transport energy for the same values of $N_t$. The following set of material parameters was used for the calculation: $\gamma = 5\ \mathrm{nm}^{-1}$, $\nu_0 = 10^{12}\ \mathrm{s}^{-1}$, $N_i = 10^{21}\ \mathrm{cm}^{-3}$, $\sigma_i = 0.08$ eV, $\sigma_t = 0.03$ eV, $E_t = 0.6$ eV.

## 7. Concluding remarks

In the present paper, we formulated a general method for considering charge-carrier hopping in disordered organic materials at weak and moderate electric fields. This method is applicable to an arbitrary DOS distribution and to an arbitrarily high density of carriers. The use of this method for consideration of carrier hopping at strong electric fields requires further work. In order to solve this problem one must consider several effects caused by strong fields, including

(i) the field effect on the energy distribution of hopping neighbours of a given starting site and
(ii) the effect of a strong electric field on the energy distribution function of localized carriers under both equilibrium and non-equilibrium conditions.

Moreover, even if these problems are resolved, it remains doubtful that one could explain the experimentally observed linear $\log \mu$ versus $\sqrt{F}$ dependence within a sufficiently broad field range. Monte Carlo simulations of carrier transport in a positionally random and energetically

disordered system of hopping sites revealed a field dependence of the mobility that can be approximated as a straight line in a log $\mu$ versus $\sqrt{F}$ plot within a narrow field range only [2]. Recently it was shown that the experimentally observed field dependence of the mobility can be explained by the occurrence of correlated hopping sites within a randomly fluctuating potential landscape [14, 15]. Therefore, application of the method developed in the present paper to carrier transport in disordered organic materials at strong fields also requires that long-range potential fluctuations be fully accounted for.

## Acknowledgments

EVE acknowledges a fellowship from the KU Leuven. This work was supported by the Stiftung Volkswagenwerk.

## References

[1] Pope H and Swenberg C E 1999 *Electronic Processes in Organic Crystals and Polymers* 2nd edn (Oxford: Oxford University Press)
[2] Bässler H 1993 *Phys. Status Solidi* b **175** 15
[3] Dieckmann A, Bässler H and Borsenberger P M 1993 *J. Chem. Phys.* **99** 8136
[4] Novikov S V and Vannikov A V 1995 *J. Phys. Chem.* **99** 14 573
[5] Miller A and Abrahams E 1960 *Phys. Rev.* **120** 745
[6] Grünewald M and Thomas P 1979 *Phys. Status Solidi* b **94** 125
[7] Monroe D 1985 *Phys. Rev. Lett.* **54** 146
[8] Scher H and Montroll E W 1975 *Phys. Rev.* B **12** 2455
[9] Movaghar B and Schirmacher W 1981 *J. Phys. C: Solid State Phys.* **14** 859
[10] Movaghar B, Grünewald B, Pohlmann B, Würtz D and Schirmacher W 1983 *J. Stat. Phys.* **30** 315
[11] Arkhipov V I, Emelianova E V and Adriaenssens G J 2001 *Phys. Rev.* B **64** 125125
[12] Arkhipov V I, Emelianova E V, Adriaenssens G J and Bässler H 2002 *J. Non-Cryst. Solids* **299–302P2** 1047
[13] Arkhipov V I, Emelianova E V and Bässler H 2001 *Phil. Mag.* B **81** 985
[14] Gartstein Y N and Conwell E M 1995 *Chem. Phys. Lett.* **245** 351
[15] Dunlap D H, Parris P E and Kenkre V M 1996 *Phys. Rev. Lett.* **77** 542