

EQUILIBRIUM HOPPING CONDUCTIVITY IN DISORDERED MATERIALS

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A general method to calculate the equilibrium hopping mobility in a positionally random and energetically disordered hopping system at weak and moderate electric fields is formulated. Analytic expressions are obtained for the equilibrium mobility controlled by an arbitrary density-of-states (DOS) distribution at arbitrarily high density of carriers. It is also shown that equilibrium charge transport occurs via carrier jumps to hopping sites located around the apparent transport level. This notion effectively reduces the variable range hopping to trap-controlled transport. The results obtained by averaging of hopping rates and by the use of the effective transport level approach are found to be in good quantitative agreement. It is also shown that multiple carrier jumps within pairs of occasionally close localized states strongly affect both the position of the effective transport energy and the equilibrium hopping mobility, especially at lower concentration of localized states.

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1. Introduction

Charge carrier transport in non-crystalline solids is well known to be governed by positional and energy disorder in such materials. The presence of positional disorder inevitably gives rise to the energy disorder via dependence of the potential energy of interaction upon the distance between interacting particles [1,2]. Due to disorder effects, carriers are almost permanently localised and the only feasible mode of charge transport is carrier jumps either via a band of extended states, if such states do occur in a given material, and/or directly between localized states. The former mechanism is often referred to as the trap-controlled transport [3] while the latter is known as hopping [4]. Trap-controlled transport implies a negligible contribution of direct tunnelling jumps of carriers between localized states compared with carrier jumps via extended states. The rate of the latter is not affected by positional disorder and, therefore, this transport mode can be considered as energy controlled hopping or \mathcal{E} -hopping. In disordered hopping systems, both positional and energy disorder affect the carrier jump rate and this transport mode is described by models of $r\mathcal{E}$ -hopping.

Most such models are based on the Miller-Abrahams [5] expression for the probability ν of a tunnelling carrier jump over the distance r between a starting state of energy E_{st} to a vacant target site of the energy E_t . This expression can be written as

$$\nu(r, E_{st}, E_t) = \nu_0 \exp(-2\gamma r) \times \begin{cases} \exp\left(-\frac{E_t - E_{st}}{kT}\right), & E_t > E_s \\ 1, & E_t < E_s \end{cases}, \quad (1)$$

where γ is the inverse localization radius of the electronic wavefunction, ν_0 the attempt-to-jump frequency, T the temperature, and k the Boltzmann constant.

The carrier jump rate exponentially decreases with increasing distance between hopping sites. At first glance it may imply that an occasionally isolated hopping site may serve as a trap for carriers. However, the rates of forward and backward jumps similarly depend upon the distance between any two hopping sites and, therefore, within a positionally random system of monoenergetic hopping sites, the carrier trapping time will be exactly equal to the release time. In other words, it is equally difficult for a carrier to be trapped and released by an isolated localized state. Nonetheless, it is not the case for an energetically random system. While upward jumps require thermal activation, downward jumps imply dissipation of the excess energy via phonon emission. The former process is much slower than the latter one and the rates of forward and backward 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. Due to this strong asymmetry of trapping and release times, the energy disorder is the main influence on charge transport characteristics in amorphous materials.

Analytic treatment of carrier hopping in a positionally random and energetically disordered system of localized states is a notoriously difficult problem. Although all jump rates are known for a fixed set of hopping sites, averaging over all possible spatial and energy configurations is not feasible. In order to resolve this problem, several simplifications of the phenomenon were introduced and approximate methods of solving the simplified problem were suggested [6-9]. Amongst these methods the concept of the effective transport level was shown to be especially efficient [10,11]. This method is based on the notion that, after an energetically upward jump into a hopping site that belongs to the transport level, a carrier will make several downward jumps, which effectively reduces hopping to trap-controlled transport [12].

It is essential for the dc conductivity that the downward jumps occur to states *other* than starting ones. This assumption is certainly valid for the trap-controlled transport but the applicability thereof for a more general case of carrier hopping in a disordered system needs special justification. Trap-controlled carrier drift and diffusion are due to carriers temporarily occupying a band of extended states. Once a carrier is released from a trap to an extended state, lots of other localised states are available for further trapping and the probability of being captured by the same trap is negligibly small. In a hopping system, a target site, which belongs to the transport level, is still a localized state that normally has only few hopping neighbours accessible for a next jump. The starting site is inevitably one of those states and it is quite possible that, after an upward jump, a carrier will return to the initially occupied deeper site. Such a jump contributes to neither dc transport nor energy relaxation.

In the present paper we formulate a general method to calculate the weak-field carrier mobility in a disordered hopping system. We also consider the influence of “multiple hopping” of carriers between occasionally close hopping neighbours on the dc hopping conductivity. The general approach will be applied to an analytical treatment of the trap-controlled hopping and hopping conductivity at large carrier densities. It is worth noting that our consideration is based on the traditional approach to hopping in disordered systems disregarding possible correlations between energies and positions of hopping sites, although such correlations may affect the field and temperature dependencies of the mobility [13,14].

2. Theory

2.1. Average hopping parameter and equilibrium carrier mobility

Since the hopping rate exponentially decreases with both increasing energy difference and increasing distance between localized states in a random system of hopping sites, most carriers will jump to target sites characterized by minimum values of the hopping parameter u , which is determined as,

$$u(r, E_{st}, E_t) = 2\gamma r + \frac{\eta(E_t - E_{st})}{kT}, \quad (2)$$

where η the unity step-function. Hereafter, such target sites will be referred to as nearest hopping neighbours. Under these conditions, the average jump rate for a carrier localized in a site of the energy E_{st} can be found by the use of the Poisson distribution [15,16]. For a starting site of energy E_{st} , the average number, $n_0(E_{st}, u)$, of hopping neighbours, whose hopping parameter is not larger than u , is given by,

$$\begin{aligned} n_0(E_{st}, u) &= 4\pi \int_0^{u/2\gamma} dr r^2 \int_{-\infty}^{E_{st}+kT(u-2\gamma r)} dE_t g(E_t) = \\ &= \frac{4\pi}{3} \left(\frac{u}{2\gamma} \right)^3 \left[\int_{-\infty}^{E_{st}} dE_t g(E_t) + \int_{E_{st}}^{E_{st}+kTu} dE_t g(E_t) \left(1 - \frac{E_t - E_{st}}{kTu} \right)^3 \right], \end{aligned} \quad (3)$$

where $g(E)$ is the density-of-states (DOS) distribution. The first term in the right-hand side of eqn. (3) gives the number of target states that are deeper than the starting site and the second one describes the number of shallower states. The former is important as far as downward carrier jumps are concerned while the latter governs the rate of upward jumps. The probability density, $w_0(E_{st}, u)$, that a nearest hopping neighbour has the hopping parameter u is determined by the Poisson distribution as,

$$w_0(E_{st}, u) = \exp[-n_0(E_{st}, u)] \frac{\partial n_0(E_{st}, u)}{\partial u}. \quad (4)$$

Equation (4) forms a basis for calculating the average hopping parameter, $\langle u \rangle_0(E_{st})$, for carrier jumps from a starting site of energy E_{st} . Using eqn. (4) as a distribution function for averaging the hopping parameter yields,

$$\langle u \rangle_0(E_{st}) = \int_0^{\infty} du u \exp[-n_0(E_{st}, u)] \frac{\partial n_0(E_{st}, u)}{\partial u} = \int_0^{\infty} du \exp[-n_0(E_{st}, u)]. \quad (5)$$

The average squared jump distance, $\langle r^2 \rangle_0(E_{st})$, can be evaluated as,

$$\begin{aligned} \langle r^2 \rangle_0(E_{st}) &= \frac{4\pi}{n_0(E_{st}, \langle u \rangle_0)} \int_0^{\langle u \rangle_0/2\gamma} dr r^4 \int_{-\infty}^{E_{st}+kT(\langle u \rangle_0-2\gamma r)} dE_t g(E_t) = \\ &= \frac{3}{5} \left(\frac{\langle u \rangle_0}{2\gamma} \right)^2 \left[\int_{-\infty}^{E_{st}} dE_t g(E_t) + \int_{E_{st}}^{E_{st}+kT\langle u \rangle_0} dE_t g(E_t) \left(1 - \frac{E_t - E_{st}}{kT\langle u \rangle_0} \right)^5 \right] \\ &\quad \times \left[\int_{-\infty}^{E_{st}} dE_t g(E_t) + \int_{E_{st}}^{E_{st}+kT\langle u \rangle_0} dE_t g(E_t) \left(1 - \frac{E_t - E_{st}}{kT\langle u \rangle_0} \right)^3 \right]^{-1}. \end{aligned} \quad (6)$$

Averaging hopping rates over E_{st} and using the Einstein relation yields the following expression for the equilibrium mobility μ_0 :

$$\mu_0 = \frac{eV_0}{kT} \int_{-\infty}^{\infty} dE_{st} \exp[-\langle u \rangle_0(E_{st})] \langle r^2 \rangle_0(E_{st}) f(E_{st}), \quad (7a)$$

where $f(E)$ is the normalized energy distribution function of localized carriers. Without dramatic loss of accuracy, rather complicated eqn. (6) for the average squared jump distance, can be replaced by a

simpler estimate $\langle r^2 \rangle_0(E_{st}) \approx \langle u \rangle_0 / 2\gamma$. This approximation yields the following formula for the equilibrium mobility μ_0 :

$$\mu_0 = \frac{eV_0}{kT(2\gamma)^2} \int_{-\infty}^{\infty} dE_{st} \exp[-\langle u \rangle_0(E_{st})] \langle u \rangle_0^2(E_{st}) f(E_{st}) . \quad (7b)$$

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 neglecting the possibility of trap filling. Under these conditions one can use a single-carrier distribution function in eqns. (7a) and (7b). The equilibrium TOF mobility can, therefore, be calculated by the use of the normalized Boltzmann distribution as,

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

Substituting this distribution function into eqn. (7a) yields,

$$\mu_0 = \frac{eV_0}{kT} \left[\int_{-\infty}^{\infty} dE_{st} g(E_{st}) \exp\left(-\frac{E_{st}}{kT}\right) \right]^{-1} \times \int_{-\infty}^{\infty} dE_{st} \exp[-\langle u \rangle_0(E_{st})] \langle r^2 \rangle_0(E_{st}) g(E_{st}) \exp\left(-\frac{E_{st}}{kT}\right) . \quad (9)$$

The results given by eqns. (7a), (7b) are obtained disregarding the possibility of backward carrier jumps into starting sites. If a carrier jump is most probably followed by the return of the carrier back to the initially occupied state both these jumps do not contribute to dc hopping transport and energy relaxation. In order to eliminate from consideration multiple carrier jumps between close hopping neighbours one must calculate the probability of a backward carrier jump.

2.2. The effect of backward carrier jumps

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 2γ *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 and r as,

$$\begin{aligned} n_b(E_t, r) &= 2\pi \int_0^r dr' r'^2 \int_{\arccos(r'/2r)}^{\pi} d\vartheta \sin \vartheta \int_{-\infty}^{E_t+2kT(r-r')} dE' g(E') = \\ &= \frac{\pi r^3}{12} \left\{ 11 \int_{-\infty}^{E_t} dE' g(E') + \int_{E_t}^{E_t+2kT\gamma} dE' g(E') \left[8 \left(1 - \frac{E'-E_t}{2kT\gamma}\right)^3 + 3 \left(1 - \frac{E'-E_t}{2kT\gamma}\right)^4 \right] \right\} . \quad (10) \end{aligned}$$

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

$$w(E_t, r) = 1 - \exp[-n_b(E_t, r)] . \quad (11)$$

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. The average number $n(E_{st}, u)$ of such hopping neighbours, therefore, can be written for upward jumps as:

$$\begin{aligned} n(E_{st}, u) &= 4\pi \int_0^{u/2\gamma} dr r^2 \int_{E_s}^{E_{st}+kT(u-2\gamma)} dE_t g(E_t) \{1 - \exp[-n_b(E_t, r)]\} = \\ &= 4\pi \int_{E_s}^{E_{st}+kTu} dE_t g(E_t) \int_0^{(1/2\gamma)[u-(E_t-E_{st})/kT]} dr r^2 \{1 - \exp[-n_b(E_t, r)]\} \end{aligned} \quad (12)$$

Average hopping parameter, $\langle u \rangle(E_{st})$, can be calculated by the use of eqn. (5), with the function $n(E_{st}, u)$ instead of $n_0(E_{st}, u)$, and average square jump distance $\langle r^2 \rangle(E_{st})$ can be evaluated from eqn. (6) using the function $\langle u \rangle(E_{st})$ instead of $\langle u \rangle_0(E_{st})$. Averaging the square jump distance over E_{st} under thermal equilibrium conditions leads to the following expression for the equilibrium mobility,

$$\mu = \frac{eV_0}{kT} \int_{-\infty}^{\infty} dE_{st} \exp[-\langle u \rangle(E_{st})] \langle r^2 \rangle(E_{st}) f(E_{st}) \quad , \quad (13)$$

that for the Boltzmann energy distribution of localized carriers leads to

$$\begin{aligned} \mu_b &= \frac{eV_0}{kT} \left[\int_{-\infty}^{\infty} dE_{st} g(E_{st}) \exp\left(-\frac{E_{st}}{kT}\right) \right]^{-1} \\ &\quad \times \int_{-\infty}^{\infty} dE_{st} \exp[-\langle u \rangle(E_{st})] \langle r^2 \rangle(E_{st}) g(E_{st}) \exp\left(-\frac{E_{st}}{kT}\right) \end{aligned} \quad (14)$$

Equation (16) is a rather complicated formula even if the expression for $\langle r^2 \rangle(E_{st})$ is replaced by its approximate value $\langle u \rangle^2/2\gamma$. The calculation of both the mobility and conductivity can be significantly simplified if the concept of the effective transport energy is employed.

2.3. Effective transport energy

The occurrence of an effective transport energy was first revealed in Monte-Carlo simulation [10] and was later proven by analytic consideration of charge carrier kinetics in disordered hopping systems [11]. In general, the probability that a jump will be made to some site of the specific energy E_t depends upon the temperature, the density-of-state distribution, the localization radius, and the energy of the starting site. However, if the DOS function is sufficiently steep and if the starting site is sufficiently deep, the most probable value of the energy E_t does not depend upon E_{st} . In other words, practically all carriers, localised in a deep tail of the DOS distribution will sooner or later 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} .

One can consider the average number of hopping neighbours as a function of the energy E_j defined as,

$$E_j = E_{st} + kTu \quad , \quad (15)$$

rather than of the hopping parameter u . Carrying out this replacement of variables in eqn. (3) yields the average number of hopping neighbours of energies not larger than E_j for a starting site of energy E_{st} :

$$n_0(E_{st}, E_j) = \frac{\pi}{6} (\gamma kT)^{-3} \int_{E_{st}}^{E_j} dE_t g(E_t) (E_j - E_t)^3 . \quad (16)$$

An upward carrier jump from a starting site is possible if there is at least one such hopping neighbour, i.e. from $n_0(E_{st}, E_j) = 1$ on. The use of this condition in eqn. (16) leads to the following transcendental equation for the energy of the most probable upward jumps:

$$\int_{E_{st}}^{E_j} dE_t g(E_t) (E_j - E_t)^3 = \frac{6}{\pi} (\gamma kT)^3 . \quad (17)$$

If the DOS distribution decreases with energy faster than $|E|^{-4}$ than (i) the value of the integral in the left-hand side of eqn. (17) is practically independent of 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_j . Physically, it means that target sites for thermally assisted upward carrier jumps are located around the energy E_j independent of the energy of starting sites and, therefore, eqn. (17) reduces to:

$$\int_{-\infty}^{E_{tr}} dE_t g(E_t) (E_j - E_t)^3 = \frac{6}{\pi} (\gamma kT)^3 . \quad (18)$$

Equation (18) for the energy of most probable jumps was derived from eqn. (3) for the average number of hopping neighbours. This equation does not account for the possibility of round-trip jumps between occasionally close hopping sites. This implies a possibility that carrier jumps to the energy E_j will be mostly followed by backward jumps to initially occupied sites. In order to preclude this possibility and obtain an equation for the genuine transport energy one should use eqn. (12) instead of eqn. (3) for the number of hopping neighbours.

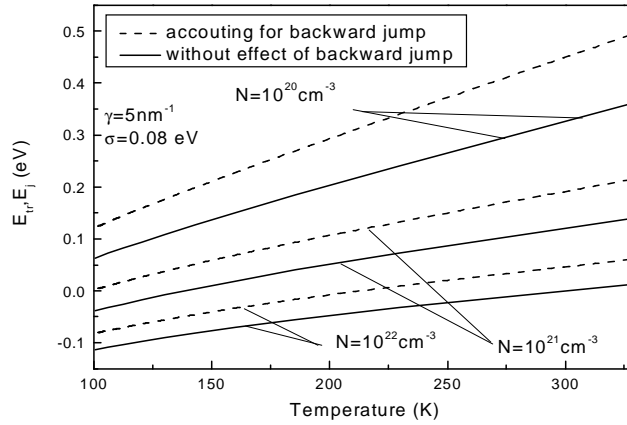


Fig. 1. Temperature dependencies of the effective transport energy and the energy of most probable jumps in a disordered hopping system with a Gaussian DOS distribution, parametric in total density of localized states N . The data shown by the solid and dashed lines are calculated from eqns. (18) and (19), respectively, for $\gamma = 5 \text{ nm}^{-1}$, and $\sigma = 0.08 \text{ eV}$.

Combining eqn. (15), in which E_j is replaced by E_{tr} , with eqn. (12) and using the condition $n(E_{st}, E_{tr}) = 1$ yields a transcendental equation for the genuine transport energy

$$4\pi \int_{-\infty}^{E_{tr}} dE_t g(E_t) \int_0^{(E_{tr}-E_t)/2kT} dr r^2 \left\{ 1 - \exp\left[-n_b(E_t, r)\right] \right\} = 1 \quad (19)$$

where $n_b(E_t, r)$ is given by eqn. (10). The energy E_{tr} is the minimum energy to which carriers must jump in order to contribute to the dc conductivity. This notion implies similarity between the effective transport level in variable-range hopping and the mobility edge in trap-controlled band transport. In general, once the effective transport energy is calculated, the hopping problem is virtually reduced to a much simpler problem of carrier multiple trapping in an energetically disordered system of localized states.

The difference between temperature dependencies of the effective transport energy and the energy of most probable jumps is illustrated in Fig. 1 for a random hopping system with a Gaussian DOS distribution of the width σ ,

$$g(E) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left(-\frac{E^2}{2\sigma^2}\right), \quad (20)$$

parametric in the density of hopping sites N . Solid lines in this figure show the temperature dependencies of the energy of most probable upward jumps calculated from eqn. (18) without accounting for backward jumps. The dashed lines were calculated from eqn. (19). The difference between dashed and solid lines for each DOS is significant and more noticeable at higher temperatures and/or at lower concentrations of localized states. Fig. 2 shows the temperature dependencies of E_j and E_{tr} calculated from eqs. (18) and (19) respectively for different widths σ of the DOS distribution. Common features of these results are that at higher temperatures the effective transport energy level lies above the maximum of the DOS distribution and that E_{tr} and E_j almost linearly increase with increasing temperature. The slopes of the curves calculated from eqn. (19) are larger than those calculated from eqn. (18).

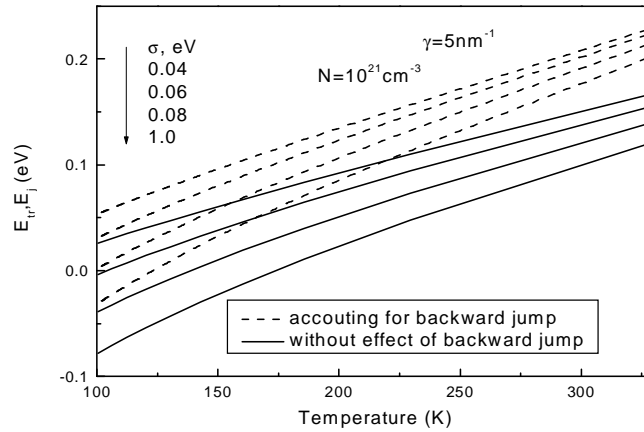


Fig. 2. Temperature dependencies of the effective transport energy and the energy of most probable jumps in a disordered hopping system with a Gaussian DOS distribution, parametric in the DOS distribution width σ . The data shown by the solid and dashed lines are calculated from eqns. (20) and (21), respectively, for $\gamma = 5 \text{ nm}^{-1}$, and $N = 10^{21} \text{ cm}^{-3}$.

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

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

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

$$\mu = \frac{eV_0}{kT} \left[\int_{-\infty}^{E_{tr}} dE g(E) \right]^{-2/3} \int_{-\infty}^{E_{tr}} dE_{st} f(E_{st}) \exp\left(-\frac{E_{tr} - E_{st}}{kT}\right). \quad (21)$$

For the single-particle Boltzmann distribution function given by eqn. (8) this expression yields

$$\mu_b = \frac{eV_0}{kT} \left[\int_{-\infty}^{\infty} dE g(E) \exp\left(-\frac{E}{kT}\right) \right]^{-1} \left[\int_{-\infty}^{E_{tr}} dE g(E) \right]^{1/3} \exp\left(-\frac{E_{tr}}{kT}\right), \quad (22)$$

where E_{tr} can be calculated either from eqn. (19) or, as a rougher approximation, from eqn. (18) that disregards the effect of round-trip carrier jumps.

It should be noted that in order to calculate the mobility described by eqns. (7a,b) or (14) one must also solve the system of eqns. (3)-(6) or (10) and (12). The expression for the equilibrium carrier mobility derived on the basis of the effective transport energy concept and given by eqn. (21) is simpler and more feasible for applications. Temperature dependences of the mobility, calculated from eqns. (7b), (18), (19), and (21) for a Gaussian DOS distribution of the width $\sigma=0.08$ eV are shown in Fig. 3 for different values of the total density of localized states N . All the curves feature almost perfect straight lines if plotted as $\log \mu$ vs $1/T^2$. Although absolute values of the mobility strongly depend upon N , the slope increases by a few percent when the density of hopping sites decreases by three orders of magnitude. The solid and dashed lines show the equilibrium mobility calculated without consideration of the round-trip hopping while the dotted curves show the effect of backward jumps. Taking into account the possibility of backward jumps leads to a significant decrease in the value of the carrier equilibrium mobility by more than two orders of magnitude especially at lower temperatures and/or lower densities of localized states. Fig. 4 shows the temperature dependences of the mobility calculated from eqns. (7b), (18), (19), and (21) for a Gaussian DOS distribution parametric in the width of the distribution.

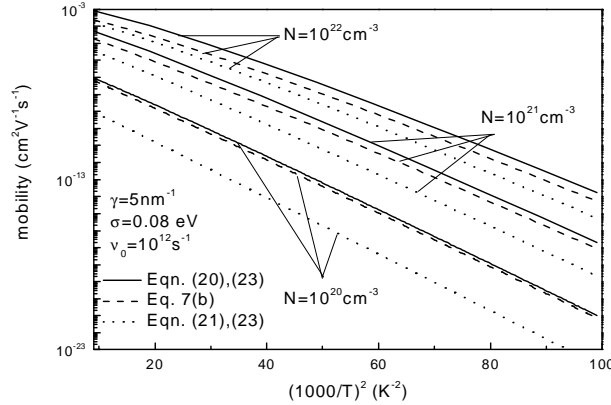


Fig. 3. Temperature dependence of the equilibrium drift mobility in a disordered hopping system with a Gaussian DOS distribution of localized states for different values of the total density of localized states N . Solid, dashed and dotted lines are calculated from eqns. (20) and (23), (7b), (21) and (23), respectively, for $\gamma = 5 \text{ nm}^{-1}$, $\sigma = 0.08 \text{ eV}$, $v_0 = 10^{12} \text{ s}^{-1}$.

2.4. The effect of high carrier density on the equilibrium hopping mobility

Electronic applications of disordered semiconductors imply high densities of the injection current and/or high doping levels in these materials. Realistic operating conditions for organic light emitting diodes (OLEDs) in active matrix colour displays are at some 500 to 1000 Cd/m^2 peak. In monochrome passive matrix displays, the peak brightness can be several 1000 Cd/m^2 . For yellow-orange, an efficiency of 10 Cd/A is typical, be it not at the highest brightness. The maximum current density in monochrome passive matrix displays is therefore of the order of several 10 mA/cm^2 to 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 hundred mA/cm². Further assuming a mobility of the order of 10⁻⁷ to 10⁻⁶ cm²V⁻¹s⁻¹, a layer thickness of 100 nm, and a voltage drop over the organic material, not including the contacts, of 5 V to 10 V depending on the colour, and a current density of several 10 to 100 mA/cm², the maximum carrier density in OLEDs can be as high as 10¹⁷ cm⁻³ to a few 10¹⁸ cm⁻³.

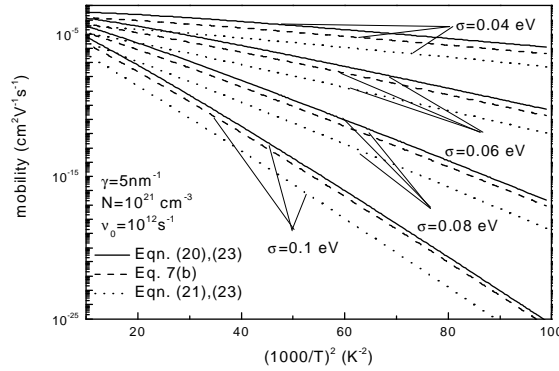


Fig. 4. Temperature dependence of the equilibrium drift mobility in a disordered hopping system with a Gaussian DOS distribution of localized states for different width of the distribution σ . Solid, dashed and dotted lines are calculated from eqns. (20) and (23), (7b), (21) and (23), respectively, for $\gamma = 5 \text{ nm}^{-1}$, $N = 10^{21} \text{ cm}^{-3}$, $\nu_0 = 10^{12} \text{ s}^{-1}$.

For organic thin film transistors, typical mobilities are much higher. For polymers, reported mobilities range between a few 10⁻³ to several 10⁻¹ cm²V⁻¹s⁻¹, while for polycrystalline materials like pentacene they range from a few 10⁻¹ to a few cm²V⁻¹s⁻¹. The typical surface carrier density accumulated under the gate insulator is of the order of 10¹² cm⁻² to 10¹³ cm⁻². The accumulated charge is localized in a sheet not thicker than a few nanometers. The carrier density in that sheet therefore turns out to be of 10¹⁸ cm⁻³ to 10¹⁹ cm⁻³.

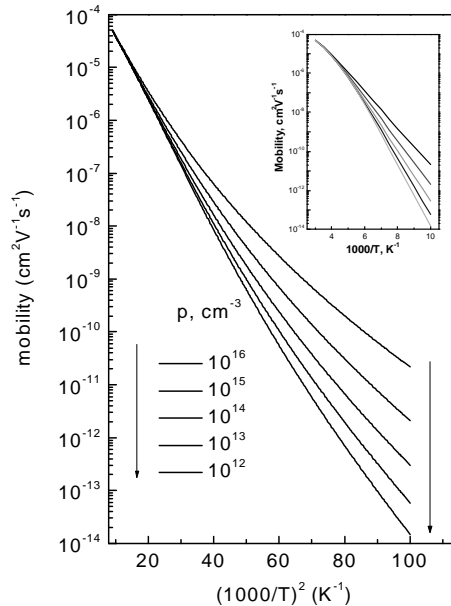


Fig. 5. Temperature dependence of the equilibrium mobility in a disordered hopping system with a Gaussian DOS distribution parametric in the carrier density for the following set of material parameters: $\gamma = 5 \text{ nm}^{-1}$, $N = 10^{21} \text{ cm}^{-3}$, $\sigma = 0.08 \text{ eV}$, $\nu_0 =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

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 dependencies of the conductivity must be sensitive to the density of charge carriers. The normalized thermally equilibrium energy distribution of localized carriers is given by a product of the Fermi-Dirac function and the DOS distribution as

$$f(E) = \frac{g(E)}{1 + \exp[(E - E_F)/kT]} \left\{ \int_{-\infty}^{\infty} \frac{dE g(E)}{1 + \exp[(E - E_F)/kT]} \right\}^{-1} \quad (23)$$

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

$$p = \int_{-\infty}^{\infty} \frac{dE g(E)}{1 + \exp[(E - E_F)/kT]} \quad (24)$$

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:

$$g_v(E) = g(E) - pf(E) = \frac{g(E)}{1 + \exp[-(E - E_F)/kT]} \quad (25)$$

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 density of states. 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 eqn. (21) with the carrier distribution function given by eqn. (23). The temperature dependence of the mobility calculated for a Gaussian DOS distribution is shown in Fig. 5 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 behavior with the activation energy decreasing with increasing carrier density as shown in the inset to Fig. 5.

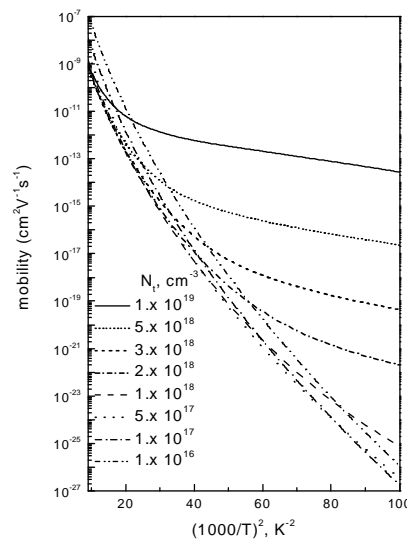


Fig. 6. The effect of deep traps on the temperature dependence of the equilibrium mobility in a disordered hopping system with a Gaussian DOS distribution. The following set of material parameters was used for the calculation: $\gamma = 5 \text{ nm}^{-1}$, $\nu_0 = 10^{12} \text{ s}^{-1}$, $N_i = 10^{21} \text{ cm}^{-3}$, $\sigma_l = 0.08 \text{ eV}$, $\sigma_s = 0.03 \text{ eV}$, $E_t = 0.6 \text{ eV}$.

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. In particular, the carrier mobility can be calculated from eqns. (12) and (13) in which the function $g(E)$ is replaced by $g_v(E)$ and the carrier distribution function is given by eqn. (23).

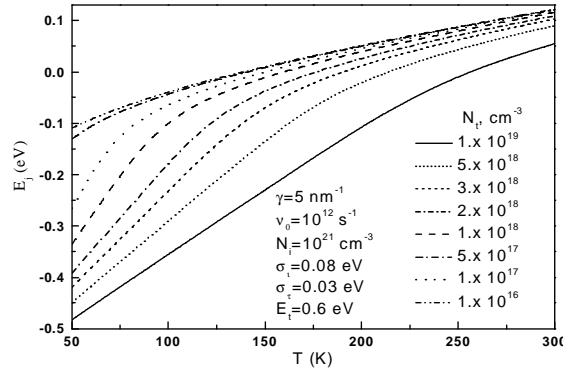


Fig. 7. The temperature dependence of the energy of most probable jumps for the same values of N_t that used in Fig. 6, for the following set of material parameters: $\gamma = 5 \text{ nm}^{-1}$, $\nu_0 = 10^{12} \text{ s}^{-1}$, $N_i = 10^{21} \text{ cm}^{-3}$, $\sigma_i = 0.08 \text{ eV}$, $\sigma_t = 0.03 \text{ eV}$, $E_t = 0.6 \text{ eV}$.

2.5. Trap-controlled variable-range hopping

In addition to the intrinsic DOS distribution, disordered organic semiconductors often have deeper localized states originating either 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. Although the total density of traps is much smaller than the density of intrinsic hopping sites, they can, especially at lower temperatures, change the effective transport energy. In addition, 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 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 a distribution of deep traps as

$$g(E) = \frac{N_i}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{E^2}{2\sigma_i^2}\right) + \frac{N_t}{\sqrt{2\pi}\sigma_t} \exp\left[-\frac{(E - E_t)^2}{2\sigma_t^2}\right], \quad (26)$$

where N_i and N_t are the total densities of intrinsic sites and traps, respectively, σ_i and σ_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 Fig. 6 for different trap concentrations. At higher temperatures, practically all carriers occupy intrinsic sites and the occurrence of traps does not change the linear $\log \mu$ vs $1/T^2$ 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 Fig. 7. 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 μ at lower temperatures.

3. Conclusions

In the present paper, we formulated a general method for considering charge carrier hopping conductivity in disordered organic and inorganic 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 carrier under both equilibrium and non-equilibrium conditions. The concept of the effective transport energy significantly simplifies consideration of the variable-range hopping of excess charge carriers. The results, obtained by the use of this approach, are relatively simple and can be readily used for calculations of device characteristics. Multiple carrier jumps between localized states, which are occasionally close neighbours in the energy-coordinate configurational space, strongly affect the effective transport energy and the equilibrium mobility in a random hopping system.

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