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On the concentration and field dependences of the hopping mobility in disordered organic solids

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Abstract

Theoretical approaches to hopping transport of charge carriers in random organic solids are considered. Concepts well approved in the field of inorganic disordered materials are claimed to be applicable to description of charge transport in random organic solids. This is illustrated by calculations of the dependence of the carrier mobility on the concentration of localized states based on the concept of transport energy. Also the widely discussed phenomenon of the mobility 'increasing with decreasing electric field at low fields' in organic materials is considered. Our calculations show that this phenomenon is likely to be an artefact caused by misinterpretation of experimental data. The concept based on the averaging of hopping rates is discussed and qualified as inappropriate.
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1. Introduction

It has been well established that hopping of charge carriers via randomly distributed localized states is the dominant transport mechanism in disordered organic solids, such as molecularly doped polymers, conjugated polymers, and organic glasses [1]. While the temperature dependence of the carrier mobility in such systems can be well described assuming a Gaussian energy distribution (DOS) of localized states [1,2], there is no agreement between researchers with respect to the appropriate theoretical description of the very key dependences of the carrier mobility μ on the concentration of localized states N and on the strength of the applied electric field E.

In all disordered organic and inorganic materials a strong non-linear dependence $\mu(N)$ is observed experimentally in the hopping regime caused by the strong exponen-

tial dependence of the transition rates v_{ij} on the distances r_{ij} between localized states:

$$v(r_{ij}, \varepsilon_i, \varepsilon_j) = v_0 \exp\left(-\frac{2r_{ij}}{\alpha} - \frac{\varepsilon_j - \varepsilon_i + |\varepsilon_j - \varepsilon_i|}{2kT}\right), \qquad (1)$$

where α is the localization length of charge carriers assumed equal for all localized states, ε_i and ε_j are energies of the initial and final states in the hopping transition, respectively, k is the Boltzmann constant, and v_0 is pre-exponential factor only slightly dependent on T and N [1,2].

While for inorganic materials the dependence $\mu(N)$ has been well described theoretically within the variable-range-hopping (VRH) approach and it has already become a subject of textbooks [3], the very same dependence $\mu(N)$ looks puzzling for many theoreticians working with organic materials. Sometimes it is claimed that dependence $\mu(N)$ in the hopping regime should be linear [4]. This conclusion is based on the ensemble averaging of hopping rates. Although this method has been already analyzed in textbooks (see, for instance, [3]) and qualified as

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inappropriate, it is still repeatedly used to describe disordered organic materials. The belief of researchers in the averaging of hopping rates is so strong that sometimes the agreement between experimental results and the exponential dependence $\mu(N)$ is called occasional, because the latter cannot be obtained by averaging of hopping rates [5]. We find it therefore useful to clarify once more the invalidity of the ensemble averaging of hopping rates for the description of hopping transport in disordered materials.

In the approach based on the averaging of hopping rates one assumes that carrier mobility is proportional to the average hopping rate $\langle v \rangle$: $\mu \propto r^2 \langle v \rangle$, where r^2 is the squared typical displacement of a charge carrier in a single hopping event [4]. The drawback of such a treatment is mostly transparent in the case of high temperatures, at which transport takes place via hopping between the nearest sites. In this regime the energy-dependent term in Eq. (1) does not play any essential role and the hopping rates are determined by spatial separations between localized states: $v(r) \approx v_0 \exp(-2r/\alpha)$. Multiplying this transition probability with the probability density to find the nearest neighbour at a given distance r, provided the total concentration of sites is N: $\varphi(r)dr = 4\pi r^2 N \exp(-4\pi r^3 N/3)dr$ and integrating over distances r one obtains for the average hopping rate the expression

$$\langle v \rangle = \int_0^\infty dr v_0 \exp\left(-\frac{2r}{\alpha}\right) \cdot 4\pi r^2 N \exp\left(-\frac{4\pi}{3}r^3 N\right)$$
$$\approx \pi v_0 N \alpha^3. \tag{2}$$

Due to the very strong decrease of the function $v(r) = v_0 \exp(-2r/\alpha)$ with increasing r at the scale $r \approx \alpha$ and due to the weak dependence of the function $\varphi(r) = 4\pi r^2 N \exp(-4\pi r^3 N/3)$ on r at $r \approx \alpha$ the average hopping rate in Eq. (2) is determined by transitions with $r \approx \alpha$. Assuming $\mu \propto r^2 \langle v \rangle$ with $r \approx \alpha$ and $\langle v \rangle$ described by Eq. (2) one comes to the result $\mu \propto N \alpha^5$ [4]. This result is however invalid for a diluted system of localized states, for which the condition $N \alpha^3 \ll 1$ should be fulfilled to justify the localization. A charge carrier cannot move over considerable distances using only transitions with the length $r \approx \alpha$ in a system with low concentration of sites $N \alpha^3 \ll 1$ [3]. Therefore the averaging of hopping rates cannot describe the charge carrier kinetic coefficients in random organic materials.

In Ref. [6] Arkhipov et al. remarked that the averaging of hopping rates used in Refs. [4] leads indeed to the omission of the concentration dependence of the carrier mobility. However, in later publications [7] the same authors claimed that the averaging of hopping rates is capable of describing the concentration dependence of the mobility. It is worth noting that the procedure called averaging of hoping rates in Ref. [7] is not the procedure called averaging of hopping rates in Refs. [4,6]. In Ref. [7] equilibrium mobility $\mu_{eq} = \sigma_{dc}/(e \cdot n)$ is considered, where n is the total concentration of charge carriers and $\sigma_{dc} = \int \mu(\varepsilon)n(\varepsilon)d\varepsilon$ is the conductivity in equilibrium conditions [8]. This value

of the equilibrium mobility is declared to be proportional to the average hopping rate: $\mu \propto r^2 \langle v \rangle$ [7]. This is therefore a new definition of the average hopping rate via the already calculated conductivity σ_{dc} as $\langle v \rangle \propto \sigma_{dc}/n$, which seems misleading being at variance to the conventional definition of the averaging procedure used in Refs. [4,6]. Furthermore, in the recent paper [9] it was claimed that the result of Ref. [4] predicting in the hopping regime the linear dependence $\mu \propto N a^5$ is correct. This situation looks confusing.

It is often claimed that in random organic solids the dependence $\mu(N)$ has the form

$$\mu \propto \exp\left\{-b\frac{N^{-1/3}}{\alpha}\right\}, \tag{3}$$

where b is a numerical coefficient [6,7]. The spread of b values in the literature is very broad. While in [6] b was estimated as $1.54 < b < 1.59$, in [7] b was claimed to be $1 < b < 1.2$ slightly depending on temperature. At $(N a^3)^{1/3} < 0.02$, this difference in b leads to the difference in μ values of more than 10 (!) orders of magnitude. Since there is no cross-citation between the papers with so different b values published in the same year by the same authors, it is not clear which value of b the authors consider as the correct one. We claim that none of these results is correct. Moreover, it has been clearly shown in straightforward computer simulations by Parris [10] that the dependence $\mu(N)$ generally cannot be represented in the form of Eq. (3) with temperature-independent coefficient b. We find it useful, therefore, to present an analytical description of the dependence $\mu(N)$, which is done in the next section following Ref. [11].

2. Calculations of $\mu(N)$

Temperature dependence of the carrier mobility in time-of-flight measurements along with computer simulations of hopping transport evidence the Gaussian shape of the DOS in disordered organic solids [1]: $g(\varepsilon) = N/\sqrt{2\pi\sigma^2} \exp\{-\varepsilon^2/(2\sigma^2)\}$. One of the most remarkable results known for energy relaxation of charge carriers in the Gaussian DOS is the transition from the dispersive character of the relaxation at early stages to the non-dispersive equilibrium regime at longer times. We present below the calculations of the drift mobility in the post-relaxation regime, in which transport is non-dispersive. The drift mobility of hopping charge carriers in such a regime can be estimated via the expression [11]

$$\ln\left\{\mu \bigg/ \left[\frac{er^2(\varepsilon_t)v_0}{kT}\right]\right\} = -2\left[\frac{4\sqrt{\pi}}{3B_C}N\alpha^3 \int_{-\infty}^{X_t/\sqrt{\pi}} \exp(-t^2)dt\right]^{-1/3}$$
$$-\frac{X_t\sigma}{kT} - \frac{1}{2}\left(\frac{\sigma}{kT}\right)^2, \tag{4}$$

where the coefficient $B_c = 2.7$ accounts for the percolation over the states with energies below the transport energy $\varepsilon_t = X_t\sigma$ and $r(\varepsilon_t)$ is the average distance between these states. The quantity X_t is determined by the equation [2]

$$\exp(X_t^2/2)\left(\int_{-\infty}^{X_t/\sqrt{2}} \exp(-t^2)\,dt\right)^{4/3}$$
$$= [9(2\pi)^{1/2}N\alpha^3]^{-1/3}kT/\sigma. \tag{5}$$

Eq. (4) determines the dependence of the carrier drift mobility on parameters $N\alpha^3$ and σ/kT. This analytical result agrees well with earlier computer simulations of Parris [10] (for comparisons see Ref. [11]).

One can show that the dependence $\mu(N)$ can be effectively represented as

$$\mu \propto \exp\{-C(N\alpha^3)^{-p}\} \tag{6}$$

with temperature-dependent parameters C and p plotted in Fig. 1. The limiting values of these parameters at very high temperatures are $C = 1.73$ and $p = 1/3$ in accord with the percolation theory [3] and computer simulations [10]. Note that this limiting value of C at $p = 1/3$ is at variance to the values of b in Eq. (3) obtained by Arkhipov et al. [6,7].

Comparison of Eq. (6) with experimental data on the dependence $\mu(N)$ [12] gives estimates $1 < \alpha < 3$ Å in various organic disordered materials. It is worth noting that comparison of Eq. (3) with the same experimental data would lead to the unreasonable conclusion that the localization length α should be temperature-dependent.

3. On the field dependence of μ at low fields

Much attention has been paid in the recent years to the dependence of the drift mobility in random organic systems on the electric field. In particular, the reported increase of the drift mobility with decreasing field at low electric fields in time-of-flight experiments [13] caused a lot of discussions in numerous review articles and modern textbooks [1,14]. In order to study this effect, we consider charge transport in a one-dimensional system. It allows one to calculate exactly the carrier transit time t_{tr} through a system of finite length at any strength of the applied electric field [15]. For numerical calculations we have chosen a chain of 2000 sites
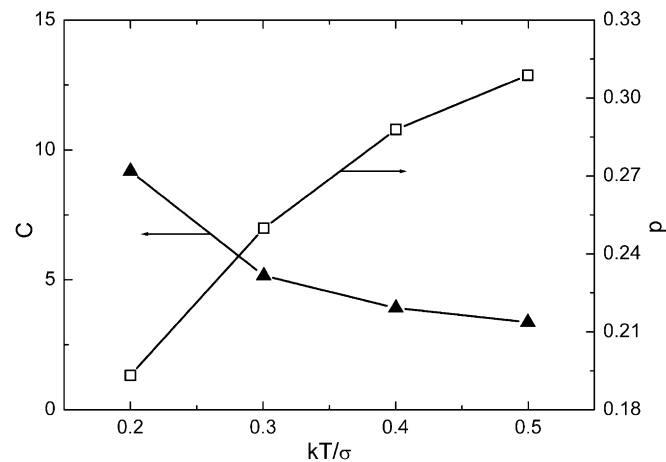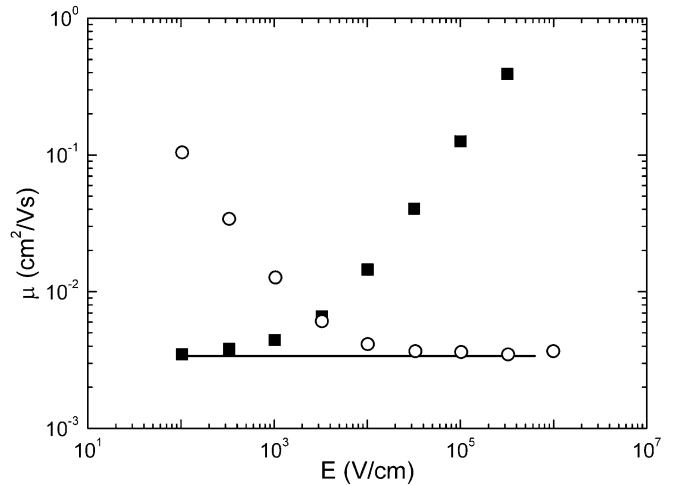

Fig. 2. Field dependence of the carrier mobility at $kT/\sigma = 0.5$. The solid line represents the exact solution for infinite chain. Data shown by circles and squares were calculated via drift and diffusion relation, respectively.

separated by 3.6 Å with decay parameter $\alpha = 1$ Å. The results shown in Fig. 2 by circles apparently demonstrate the increase of the mobility with decreasing electric field E. These results were obtained via the standard formula for drift mobility $\mu = L/(t_{tr}E)$, where L is the length of the sample. This formula was also used in experimental work [13]. However at low electric fields the transit time is not necessarily determined by drift of charge carriers. Even at zero electric field the carriers would penetrate through the finite system solely due to diffusion. Therefore we tried at low fields also the diffusion formula $\mu = (e/kT)L^2/(2t_{tr})$. The result is shown in Fig. 2 by squares. The remarkable feature of this result is the coincidence between μ values at low fields obtained via the diffusion formula with those at higher fields obtained via the drift formula. This coincidence suggests that at low fields diffusion processes are responsible for the carrier transients and the mobility does not increase with decreasing field. It also suggests that the conclusion on the mobility increasing with decreasing field [1,13,14] might be an artefact caused by neglecting the diffusive nature of the transient processes at low electric fields in the interpretation of time-of-flight data in finite samples. The transition from the diffusion-limited transport to the drift-limited regime occurs when electrostatic potential (the external one plus the built-in one) across the sample exceeds the values kT/e [16]. This idea has been also suggested in Ref. [17] on the basis of experimental study.

4. Conclusions

Theoretical study of charge carrier hopping transport in disordered organic solids with a Gaussian DOS shows that these processes can be well described theoretically by traditional methods well approved for inorganic disordered solids. In particular, the variable-range-hopping is responsible for the dependence of the carrier mobility on the concen-

Fig. 1. Temperature dependences of the parameters C and p in Eq. (6).

tration of localized states. A comparison of the theoretical result (Eq. (6)) with experimental data provides a reasonable estimate for the localization length α. Results of the exact calculations in one-dimensional systems suggest that the widely discussed phenomenon of the mobility increasing with decreasing electric field might be caused by misinterpretation of the time-of-flight experimental data, in particular, by neglecting the contribution of diffusion processes to charge transport at low fields. It is also emphasized that averaging of hopping rates is not an appropriate method to describe hopping transport in disordered systems.

Acknowledgements

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