Concentration dependence of the transport energy level for charge carriers in organic semiconductors

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The concept of the transport energy (TE) has proven to be one of the most powerful theoretical approaches to describe charge transport in organic semiconductors. In the recent paper Li *et al.* [APL **92**, 013307 (2008)] have studied the effect of the partially filled localized states on the position of the TE level. We show that the position of the TE is essentially different to the one suggested by Li *et al.*. We further modify the standard TE approach taking into account the percolation nature of the transport path. Our calculations show that the TE becomes dependent on the concentration of charge carriers n at much higher n values than those, at which the carrier mobility already strongly depends on n. Hence the calculations of the concentration-dependent carrier mobility cannot be performed within the approach, in which only the concentration dependence of the TE is taken into account.

Since most of the realized organic electronic devices are based on thin amorphous or polycrystalline layers, it is of vital importance to have an adequate theoretical description of charge transport in such materials. In disordered organic systems charge transport occurs via incoherent hopping of carriers (electrons or holes) between strongly localized states with Gaussian energy distribution[1–7]:

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

where N is the total concentration of localized states and σ is the energy scale of the order of $0.1eV$[1–6]. The hopping transition rate for a charge carrier from an occupied localized state i to an empty localized state j over a distance r_{ij} is described by the Miller-Abrahams expression:

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{a}\right) \exp\left(-\frac{\varepsilon_j - \varepsilon_i + |\varepsilon_j - \varepsilon_i|}{kT}\right), \tag{2}$$

where a is the localization length, which is assumed equal for sites i and j, and the preexponential factor ν_0 depends on the interaction mechanism that causes transitions[3–6,8]. In the case of thermal equilibrium, which we consider, the energy distribution of carriers is described by the Fermi function with the Fermi level ε_F determined by the condition

$$\int_{-\infty}^{\infty} \frac{g(\varepsilon)d\varepsilon}{1 + \exp[(\varepsilon - \varepsilon_F)/kT]} = n, \tag{3}$$

where n is the concentration of charge carriers. Eqs. (1)-(3) formulate a self-consistent theoretical problem with three parameters: σ/kT, Na^3 and n/N.

In spite of the broad agreement between researchers on the validity of this model for organic semiconductors, mathematical solutions of the transport problem suggested so far are rather controversial. This situation is particularly unsatisfactory since in the parallel field of inorganic disordered materials well-approved theoretical methods have been developed for decades. These methods are the percolation theory[9] and the concept of transport energy (TE)[10–12]. In contrast, in the field of organic materials it is widely believed that for Gaussian density of states (DOS) analytical theories are not possible and the only theoretical method to study charge transport are computer simulations[1,3,13].

In fact, analytical theories for organic materials with Gaussian DOS can be developed much easier than those for inorganic materials where the DOS depends on energy exponentially or even weaker. In the latter case, in an empty system charge carriers dive in

energy unlimitedly in course of time[6]. The speed of spatial charge carrier motion slows down in time and the transport coefficients appear time-dependent. This regime is called the dispersive transport. In this regime the carrier mobility μ always depends on the concentration of carriers n, since the diving in energy stops when the energy position of charge carriers arrives in the vicinity of the n-dependent Fermi level. Therefore it is surprising for researchers experienced with inorganic disordered systems that the dependence $\mu(n)$ is being so much highlighted for organic materials[14,15]. On the contrary, it could be considered surprising that at low carrier concentrations the carrier mobility does not depend on n in organic materials. The reason for this independence is the following. In the Gaussian DOS, even if the system is empty, a carrier does not dive in energy unlimitedly in course of time. Instead in the equilibrium conditions it spends most time in the vicinity of the so-called equilibrium energy[1,6] ε_∞:

$$\varepsilon_\infty = \frac{\int_{-\infty}^{\infty} \varepsilon g(\varepsilon) \exp(-\varepsilon/kT) d\epsilon}{\int_{-\infty}^{\infty} g(\varepsilon) \exp(-\varepsilon/kT) d\epsilon} = -\frac{\sigma^2}{kT}. \tag{4}$$

This feature gives the carrier mobility a definite value[16] even in the empty system when $\varepsilon_F(n) < \varepsilon_\infty$. Mobility becomes n-dependent only at such high concentrations that[7,17,18] $\varepsilon_F(n) \geq \varepsilon_\infty$. The critical concentration n_c, above which mobility becomes dependent on the carrier concentration n is determined by the condition[7,17] $\varepsilon_F(n_c) = \varepsilon_\infty$, which gives[18]

$$n_c = \frac{N}{2} \exp\left(-\frac{\sigma^2}{2(kT)^2}\right). \tag{5}$$

Let us estimate the critical concentration n_c for real conditions. Taking the value $\sigma \simeq 0.1eV$[1-6] we will use for room temperatures, $kT \simeq 0.025eV$, the magnitude $\sigma/kT = 4$. Inserting this parameter into Eq. (5) we obtain the relative concentration $n_c/N \approx 1,7\cdot10^{-4}$, above which the carrier mobility becomes n-dependent. In Fig. 1 we plot the dependence $\varepsilon_F(n)$ calculated via Eq. (3) along with the position of the equilibrium energy ε_∞ for $\sigma/kT = 4$. It is clearly seen that for $n/N > 10^{-3}$ the Fermi level $\varepsilon_F(n)$ is situated essentially higher than ε_∞ so that the low-concentration limit based on the approximation that most carriers stay in the vicinity of ε_∞, fails.

Monte Carlo computer simulations[1,20] within the model described by Eqs. (1), (2) showed at small n the temperature dependence of the mobility in the form

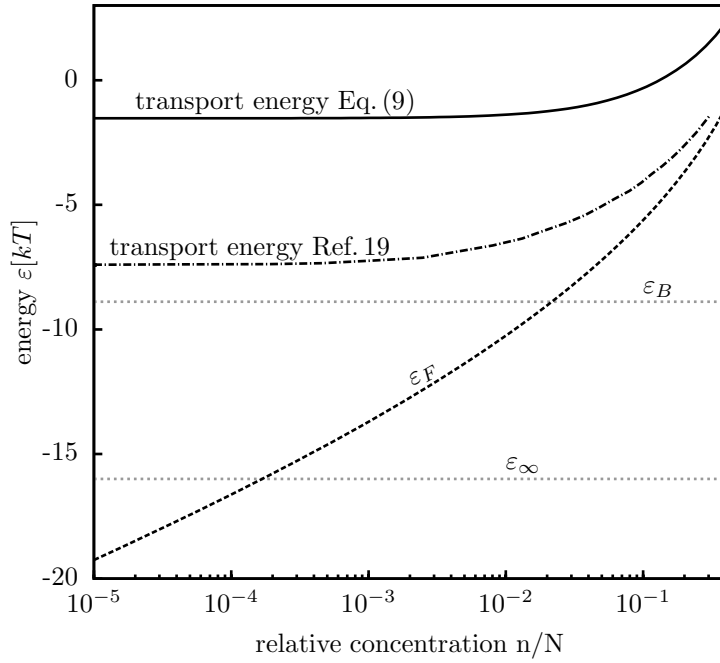$$\mu \propto \exp\left(-C\left(\frac{\sigma}{kT}\right)^2\right) \tag{6}$$

FIG. 1. The transport energy in units of kT vs. the relative charge carrier concentration n/N. Solid line: the result of Eq. (9); dashed-dotted line: the result of Ref. 19. The positions of the Fermi level, ε_F, of the equilibrium energy, ε_∞ and that of $\varepsilon_B = -5/9(\sigma^2/kT)$ are also plotted. The parameters are $\sigma/kT = 4$ and $Na^3 = 0.01$.

with $C \simeq 4/9$. This result seemed independent on the parameter Na^3 since this parameter has not been varied in the simulations[1,20]. Furthermore, this result along with the belief[1,21] that moving carriers are activated to the transport path from the energy ε_∞ determined by Eq. (4) brought many researchers[1,21,22] to the erroneous conclusion that the energy responsible for charge carrier motion in a Gaussian DOS, i.e. the TE, is $\varepsilon_B \simeq -(\frac{\sigma^2}{kT}) + 4/9(\frac{\sigma^2}{kT}) = -5/9(\frac{\sigma^2}{kT})$. Position of this energy ε_B is shown in Fig. 1. Our calculations of the TE given below show however that the energy level ε_B has nothing to do with the real position of the TE.

One should emphasize that activation of charge carriers to the TE occurs not from ε_∞ but rather from the Fermi level[6,7,17]. For the diluted systems studied in computer simulations[1] Eq. (3) gives for ε_F the temperature dependence[17]

$$\varepsilon_F = -\frac{1}{2}\left(\frac{\sigma^2}{kT}\right) - kT\ln\left(\frac{N}{n}\right). \tag{7}$$

The difference of the coefficient $C \simeq 4/9$ in Eq. (6) obtained in the computer simulations[1] from the factor $1/2$ in the first term in the r.-h. side of Eq. (7) is due to the temperature

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dependence of the TE.

The dependences of the TE on parameters σ/kT and Na^3 for the Gaussian DOS have first been calculated[16,23] in the way completely analogous to the calculations of the TE for exponential DOS[12]. In these calculations one searches for the target energy for electron hops that maximizes the transition rate. As a result the energy ε_t has been found[16,23] so that for localized states with energies lower than ε_t the fastest hop brings carriers to the vicinity of ε_t, while for states with energies above ε_t the favorable hop is a transition downward in energy to the nearest in space localized state. Recently Li et $al.$ have mentioned[19] that the derivation of the TE ε_t performed in Refs. 16 and 23 can be valid only for a diluted system of carriers when the filling of localized states can be neglected. Li et $al.$ performed the derivation of ε_t literally in the same form as in Refs. 16 and 23 though with one improvement. Calculating the typical distance to the target cite in a hopping event via the concentration of states below the target energy ε, Li et $al.$ used the expression[19]

$$R(\varepsilon) = \left(\frac{4\pi}{3}\int_{-\infty}^{\varepsilon} g(\varepsilon')[1 - f(\varepsilon', \varepsilon_F)]\,d\varepsilon'\right)^{-1/3}, \tag{8}$$

where $f(\varepsilon, \varepsilon_F)$ is the Fermi function, while in Refs. 16 and 23 the value $f(\varepsilon, \varepsilon_F) = 0$ was used assuming that the concentration of carriers is low. The results given by Li et $al.$ for $\sigma/kT = 4$ and $Na^3 = 0.01$ in Ref. 19 are shown in Fig. 1 by the dashed-dotted line.

With respect to deriving a comprehensive equation for the TE it is necessary to note the following. If in a search for the value of the TE one uses the hopping distance given by Eq. (8) one neglects the percolation nature of the hopping transport. In order to have a connected transport path for the dc conduction, the average number of empty sites B within the hopping distance should not be unity as supposed in Eq. (8), but rather[9] $B = 2.7 \pm 0.1$. The necessity to take this percolation criterion into account for hopping transport in organic materials is well-known[17,18,24]. It can be done using the factor $4\pi/B$ instead of 4π in Eq. (8). Literally following the calculations from Ref. 16 and 23 using Eq. (8) we obtain within the percolation approach the following equation for the concentration-dependent transport energy $\varepsilon_t = \sigma \cdot x$

$$(1 + \exp(\frac{\varepsilon_F - \sigma x}{kT}))e^{x^2/2}\left(\int_{-\infty}^{x/\sqrt{2}} \frac{e^{-t^2}\,dt}{1 + \exp(\frac{\varepsilon_F - \sqrt{2}\sigma t}{kT})}\right)^{4/3}$$
$$= (9\sqrt{2\pi}B^{-1}Na^3)^{-1/3}\frac{kT}{\sigma}. \tag{9}$$

This equation differs from the corresponding equation by Li *et al.*[19] (Eq. (8) in Ref. 19) in two respects. First, the percolation nature of hopping transport is taken into account in Eq. (9) via the percolation threshold B. Second, the integration variable t appears in the argument of the exponential function in the denominator under the integral in Eq. (9), while this variable in Eq. (8) by Li *et al.*[19] is replaced by the dimensionless magnitude of the transport energy x. We do not see any reason for the latter replacement. Numerical solution for the TE via Eq. (9) for parameters $\sigma/kT = 4$ and $Na^3 = 0.01$ as used by Li *et al.* is shown in Fig. 1 by the solid line. This result is remarkable in at least three respects. First, it is at a strong variance to the result of Li *et al.*[19] also shown in the Fig. 1 by the dashed-dotted line. Second, our result shows that the transport path is situated for realistic parameters in a close vicinity of the maximum of the Gaussian DOS. Such transport picture has been assumed in the literature (see, for instance, Ref. 25) though without rigorous justification. Our calculations justify this assumption. Third, the result of Eq. (9) shows that the TE is essentially independent of the concentration of charge carriers n up to rather high concentrations $n_t \approx 0.05N$.

The question arises now on how to calculate the carrier mobility $\mu(n)$ using this result for the TE. Li *et al.*[19] suggest to use for this purpose Eq. (13) from Ref. 16 taking into account only the concentration dependence of the TE. It is necessary to emphasize, however, that the idea of calculating the carrier mobility via Eq. (13) by Baranovskii *et al.*[16] is valid only for diluted systems with low carrier concentration $n < n_c$. The result of Eq. (9) evidences however that the concentration, at which the TE becomes dependent on n is essentially higher than n_c. In the whole range of concentrations n, in which the TE depends on n the carrier mobility $\mu(n)$ cannot be calculated by Eq. (10) in Ref. 19 derived by Baranovskii *et al.*[16] for diluted systems. At concentrations n larger than n_c the carrier mobility should be instead calculated as[6,17] $\mu(n) = \Sigma(n)/(e \cdot n)$, where $\Sigma(n)$ is the concentration-dependent conductivity.

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