Concentration dependence of the hopping mobility in disordered organic solids

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It has already become a tradition in the field of disordered organic solids to plot the dependence of the carrier mobility μ on the concentration of localized states N in the form $\mu \propto \exp[-C(N\alpha^3)^{-p}]$ with $p=1/3$ and constant C. Moreover, it is this concentration dependence that is usually employed in order to determine experimentally the localization length of charge carriers α from the plots $\ln(\mu)$ versus $N^{-1/3}$. We study the $\mu(N)$ dependence theoretically and show that both parameters p and C are not universal and that they essentially depend on temperature. This result is general and it shows that the estimate of the wave function decay α employing the dependence $\mu(N)$ should be based on the appropriate theory which takes into account the temperature dependences of the parameters p and C. Results are compared with those of computer simulations and with experimental data.

I. INTRODUCTION

Organic photoconductors, such as conjugated and molecularly doped polymers and organic glasses represent a rapidly evolving research area due to their current and potential applications in various electronic devices.[1–3] In particular, the transport properties of the charge carriers are widely studied. The central transport quantity is the mobility μ of the charge carriers, which in most cases is determined by incoherent hopping processes among a system of localized electronic states. It thus depends on details of the wave functions and on the concentration N of the localized states. Usually this dependence is represented in the form

$$\mu \propto \exp[-C(N\alpha^3)^{-p}], \tag{1}$$

with constant C and $p=1/3$.[4–10] In this formula α is the decay length of the carrier wave function in the localized states. Equation (1) with $C=2$ is often used to determine α from the experimental plots of $\ln(\mu)$ versus $N^{-1/3}$.[5,7] This value $C=2$ is taken from the Miller-Abrahams expression for the jump rate describing the transition of the charge carrier from an occupied localized state i to an empty localized state j:[11]

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{\alpha}\right) \exp\left(-\frac{\epsilon_j - \epsilon_i + |\epsilon_j - \epsilon_i|}{2kT}\right). \tag{2}$$

Here ϵ_i and ϵ_j are the energies of the localized states on sites i and j, respectively; r_{ij} is the distance between the sites; ν_0 is the attempt-to-escape frequency; k is Boltzmann's constant. At high enough temperatures the energy-dependent factor in Eq. (2) does not play a significant role and the hopping rate is determined by the tunneling probability $\exp(-2r_{ij}/\alpha)$. For the calculation of a typical hopping rate, the intersite distance r_{ij} was estimated to be $N^{-1/3}$, which leads to Eq. (1) with $C=2$ and $p=1/3$.

In fact, this is a very rough estimate for the $\mu(N)$ dependence even in the case of the so-called r-hopping regime

where the energy-dependent factors in Eq. (2) are neglected. A more precise formula is based on percolation theory.[12] According to the percolation approach, one should find the shortest distance r_c which opens an infinite path through the system via sites separated by distances smaller than r_c. Then the estimate for the drift mobility μ is $\mu \propto \exp(-2r_c/\alpha)$.[12] Percolation theory gives the value $r_c \approx 0.865 N^{-1/3}$ leading to Eq. (1) with $p=1/3$ and $C \approx 1.73$.[12] Such a dependence should be expected at very high temperatures in the so-called nearest-neighbor-hopping (NNH) regime. In this regime the jump rates do not depend on the energy factors in Eq. (2) and thus the drift mobility of charge carriers does not depend on temperature. However, the hopping drift mobility of carriers in organic disordered solids shows a strong temperature dependence and hence the transport process should be described by a variable-range-hopping (VRH) approach rather than by the NNH. The dependence $\mu(N)$ with $p=1/3$ and $C=1.73$, though being inherent in the NNH approach, is hardly to be expected for the VRH. Kinetic coefficients in the VRH are known to be determined by the interplay between spatial and energy terms in the transition probabilities and a more sophisticated dependence $\mu(N)$ should be expected.[12] Of course, this interplay is significant only if a pronounced temperature dependence of kinetic coefficients is observed. This is the case in organic materials at temperatures used in the experimental studies.[1–3,13]

Straightforward computer simulations have shown that the experimentally observed temperature dependence of the drift mobility, $\mu \propto \exp[-(T_0/T)^2]$, gives evidence for the energy distribution of localized states (DOS) in organic disordered media to be Gaussian:[2,3]

$$g(\epsilon) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\epsilon^2}{2\sigma^2}\right). \tag{3}$$

Here N is the total concentration of localized states and σ is the energy scale of the energy distribution.

The dependence of the carrier drift mobility μ on the concentration of localized states N in a system of random sites with a Gaussian DOS has also been studied by computer simulations.[14] To obtain this dependence we here suggest an analytical approach that is based on exactly the same model which was underlying the computer simulations:[2,14] a random distribution of localized states with a Gaussian DOS. Although numerous claims in review papers[2,3] state that a model with Gaussian DOS does not lead to closed analytical solutions for transport problems, an analytical theory for hopping transport in disordered systems with Gaussian DOS has in fact been developed recently.[15] The theory is based on the concept of the transport energy. It is shown to be valid for the description of hopping transport under low electric fields in random systems with Gaussian DOS.[16] Though approximate, the theory provides temperature dependences for the drift mobility and for the equilibration time of hopping charge carriers in good agreement with computer simulations.[15] Below we apply this theoretical approach to calculate the concentration dependence of the carrier drift mobility. We show that, as expected for the VRH, the dependence $\mu(N)$ is weaker than $\ln(\mu) \propto N^{-1/3}$ and, more important, it essentially depends on temperature. Equation (1) with $p \approx 1/3$ appears to be only approximately valid for restricted ranges of parameters kT/σ and $N\alpha^3$.

II. THEORY

In order to calculate the drift mobility μ of charge carriers in a disordered system characterized by an exponentially broad distribution of local transition probabilities given by Eq. (2) one should average the hopping times over the ensemble of transitions performed by a mobile charge carrier.[15] This recipe becomes transparent if one takes into account that, according to the Miller-Abrahams approach, the hopping time of a charge carrier between two localized states is analogous to the local resistance inserted between the two sites.[11,12] By averaging the hopping times over the transitions one simply averages the resistances connected sequentially. Such averaging is an easy exercise provided one knows the path the charge carrier takes in real space. Fortunately, there is a transparent way to reveal this path using the well-approved concept of the transport energy. This concept is valid for systems with a steep energy distribution of localized states, though it is not applicable for systems with a smooth DOS (Ref. 16). It has been first suggested for systems with exponential DOS (Ref. 17) and later extended to systems with a Gaussian DOS.[16] According to this concept, a particular energy level ϵ_t, called by Monroe the transport energy,[17] determines each single hopping event of carriers situated energetically deeper than ϵ_t. Qualitatively hopping transitions of charge carriers in energy space look as follows. From energy levels above ϵ_t, carriers fall down via hops to spatially neighboring sites with lower energies. On the other hand, from levels below ϵ_t, the carriers perform upward jumps to the close vicinity of the transport energy ϵ_t and sequentially fall down to deeper energy levels. Hence, every second jump brings a carrier upward to the vicinity of ϵ_t being succeeded by a jump to a deeper level with an energy

determined solely by the DOS energy distribution. Therefore, in order to calculate the drift mobility μ, it is correct to average the times of hopping transitions over the DOS function for states below ϵ_t because only these states are essential for transport.[15] Hops downward in energy from the level ϵ_t occur exponentially faster than upward hops towards ϵ_t. Therefore one can neglect the former in the calculation of the average time $\langle t \rangle$. The carrier drift mobility can be evaluated as[15]

$$\mu \sim (e/kT)R^2(\epsilon_t)\langle t \rangle^{-1}, \tag{4}$$

where e denotes the elementary charge and $R(\epsilon_t)$ is the typical length of hopping transitions to ϵ_t from lower-energy states determined by the concentration of localized states below ϵ_t:

$$R(\epsilon_t) = \left[\frac{4\pi}{3} \int_{-\infty}^{\epsilon_t} g(\epsilon) \, d\epsilon \right]^{-1/3}. \tag{5}$$

The average hopping time has the form

$$\langle t \rangle = \nu_0^{-1} \int_{-\infty}^{\epsilon_t} \exp\left(\frac{2R(\epsilon_t)B^{1/3}}{\alpha} + \frac{\epsilon_t - \epsilon}{kT} \right)$$
$$\times g(\epsilon) \, d\epsilon \left[\int_{-\infty}^{\epsilon_t} g(\epsilon) \, d\epsilon \right]^{-1}, \tag{6}$$

where $B \approx 2.7$ is the percolation parameter. This numerical coefficient is introduced into Eq. (6) in order to warrant the existence of an infinite percolation path over the states with energies below ϵ_t. The transport energy ϵ_t is determined as

$$\epsilon_t = \sigma x_t(N\alpha^3, kT/\sigma), \tag{7}$$

with $x_t(N\alpha^3, kT/\sigma)$ being a solution of the equation[15]

$$\exp\left(\frac{x^2}{2} \right) \left[\int_{-\infty}^{x/\sqrt{2}} \exp(-t^2) \, dt \right]^{4/3} = \frac{kT}{\sigma} (9\sqrt{2\pi}N\alpha^3)^{-1/3}. \tag{8}$$

One can neglect the concentration dependence of the prefactor $(e/kT)[R(\epsilon_t)]^2$ in Eq. (4) compared to the exponential term in $\langle t \rangle$. Substituting Eqs. (5)–(8) into Eq. (4) one obtains for the drift mobility

$$\ln\{\mu/[eR^2(\epsilon_t)/kT]\}$$
$$= -2\left[\frac{4\sqrt{\pi}}{3B} N\alpha^3 \int_{-\infty}^{x_t/\sqrt{2}} \exp(-t^2) \, dt \right]^{-1/3}$$
$$- \frac{x_t}{kT/\sigma} - \frac{1}{2(kT/\sigma)^2}. \tag{9}$$

It is Eq. (9) that determines the dependence of the carrier drift mobility on parameters kT/σ and $N\alpha^3$. The mathematical approach described above is valid for a range of these parameters corresponding to rather low ϵ_t values: $\epsilon_t \leq -\sigma/2$, since the relation between $R(\epsilon_t)$ and ϵ_t given by Eq. (5) breaks down for higher ϵ_t.[15] In what follows we present results only for $\epsilon_t \leq -\sigma/2$.
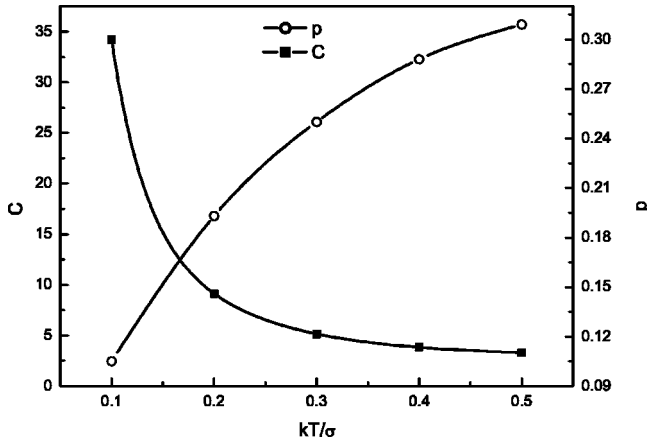
FIG. 1. Temperature dependences of the parameters C and p in Eq. (1).

FIG. 2. Concentration dependence of the drift mobility for different values of kT/σ.

So far most attention of researchers has been devoted to the temperature dependence of the drift mobility.[2,3] Equation (9) has been shown to describe this temperature dependence in agreement with experimental data and computer simulations.[15] In the present work we study the dependence of the drift mobility μ on $N\alpha^3$ keeping kT/σ as a parameter. Although Eq. (9) does not provide a pure power law for the dependence of $\ln(\mu)$ on $N\alpha^3$, we will always try to represent the concentration dependence of the carrier drift mobility in the form of Eq. (1) aiming at a comparison of our theoretical results with experimental data.

According to numerous experimental studies of the temperature dependence of the drift mobility in various organic disordered solids, particularly in doped polymers, the width σ of the DOS energy distribution in such systems varies from 0.065 to 0.150 eV depending on the kind of dopant, dopant concentration, and host polymers.[3] The temperature in the experimental studies was taken between 200 K and 350 K.[3] Hence the values of the parameter kT/σ in the experiments fall in the range between 0.1 and 0.5. In what follows we will analyze the dependence of $\ln(\mu)$ on $N\alpha^3$ for kT/σ in the range between 0.1 and 0.5.

In Fig. 1 we show the values of parameters p and C that provide the best fit for the solution of Eq. (9) in the form of Eq. (1). These data were calculated for $N\alpha^3$ in the range $0.001 < N\alpha^3 < 1.0$. It is well seen in Fig. 1 that for low enough temperatures the values of the parameter p are less than $1/3$. This is to be expected for the VRH transport mechanism based on the interplay between the spatial and energy factors in the exponent of the transition probability given by Eq. (2).[18] Energy-dependent terms in Eq. (2) diminish the effect of the spatially dependent terms in the expression for the transition probability and they lead to a weaker dependence of the carrier mobility on $N\alpha^3$ compared to the NNH regime with $p = 1/3$, in which only spatial terms determine the mobility. The values of p in Fig. 1 obtained for a Gaussian DOS differ from the value $p = 1/4$ in Mott's law which is valid for the energy-independent DOS.[18] The concentration dependence of the drift mobility in the form of Eq. (1) with parameters p and C given in Fig. 1 is the main result of our report.
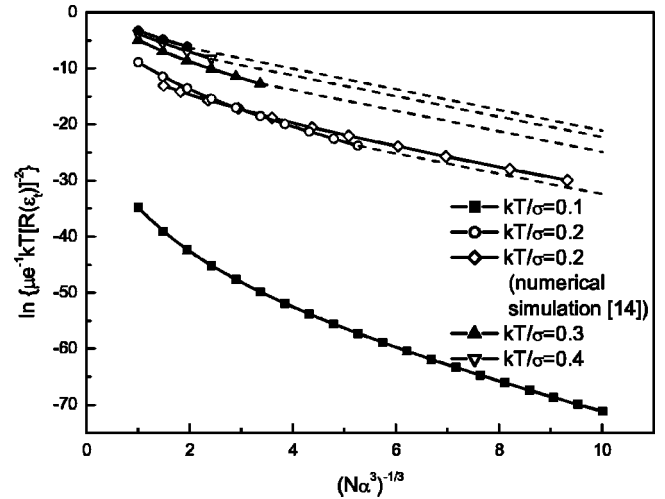
III. DISCUSSION

Data plotted in Fig. 1 raise the question, how was it possible to plot numerous experimental data in the form of Eq. (1) with $p = 1/3$ for kT/σ essentially smaller than 0.5? In order to answer this question, we plot in Fig. 2 the values of $\ln(\mu)$, obtained by solving Eq. (9), versus $(N\alpha^3)^{-1/3}$. The dashed parts of the curves correspond to parameter values at which the concept of the transport energy cannot be straightforwardly justified, while the solid parts of the curves represent reliable results. It is well seen, in particular, for small kT/σ values that $\ln(\mu)$ is not a linear function of $(N\alpha^3)^{-1/3}$. This nonlinearity has first been obtained theoretically in computer simulations carried out by Parris.[14] In Fig. 2 we compare the slopes obtained from our analytic calculations with those from computer simulations of Parris at $kT/\sigma = 0.2$. The agreement between our data and the results of numerical simulations confirm the validity of our analytical approach.

In fact, experimental data in Refs. 5, 7, and 8 show the same curvature of the $\ln(\mu)$ versus $(N\alpha^3)^{-1/3}$ plots as do our theoretical results in Fig. 2. In Fig. 3 we plot the values of $\ln(\mu)$, obtained by solving Eq. (9), along with experimental data for the drift mobility in TNF/PVK and TNF/PE (Ref. 8) as a function of $N^{-1/3}$. In such plots it is not possible to fit the data by a straight line in the whole range of concentrations. This obvious curvature in the experimental data has been, however, neglected so far.

The values of the slope parameter C in Eq. (1) which are plotted in Fig. 4 yield an approximate presentation of the dependence of $\ln(\mu)$ on $N\alpha^3$ in the form of Eq. (1) with $p = 1/3$. The strong dependence of C on $N\alpha^3$ gives evidence that Eq. (1) is a rather poor description of the concentration dependence of the drift mobility. Although the data shown in Figs. 1–4 in general exclude the use of Eq. (1) for the concentration dependence of the charge carrier drift mobility, one can fit the data for $\ln(\mu)$ in Fig. 2 by a linear function of $(N\alpha^3)^{-1/3}$ in a restricted range of $N\alpha^3$. This is apparently the reason why, on the basis of experimental data, it has not been recognized so far that Eq. (1) with $p = 1/3$ and constant
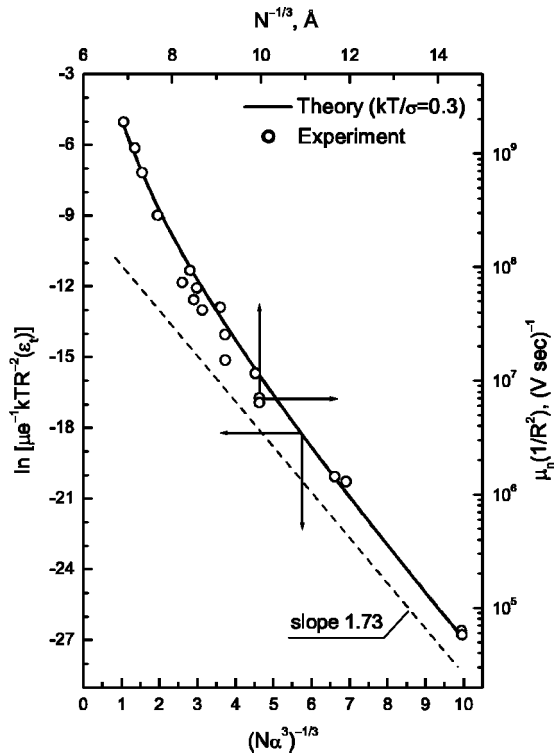
FIG. 3. Concentration dependence of the drift mobility evaluated from Eq. (9) for $kT/\sigma = 0.3$ (solid line) and the one observed in the experiment (circles) for TNF/PE and TNF/PVK.[8]

FIG. 4. Concentration dependence of the factor C (assuming $p = 1/3$) in Eq. (1) for different values of kT/σ. The dashed-dotted line corresponds to the value $C = 1.73$ valid for the NNH.

'C does not provide a correct description of the concentration dependence of the drift mobility. In lack of a more reliable theory one was lead to use the simplistic version of Eq. (1) with $C = 2$ and $p = 1/3$ in order to fit the data.[5,7,8]

In Table I we present estimates for the decay parameter α of the localized carrier wave function for various molecularly doped polymers studied in Refs. 5, 7–9. The estimates were performed on the one hand by using Eq. (1) with $p = 1/3$ and
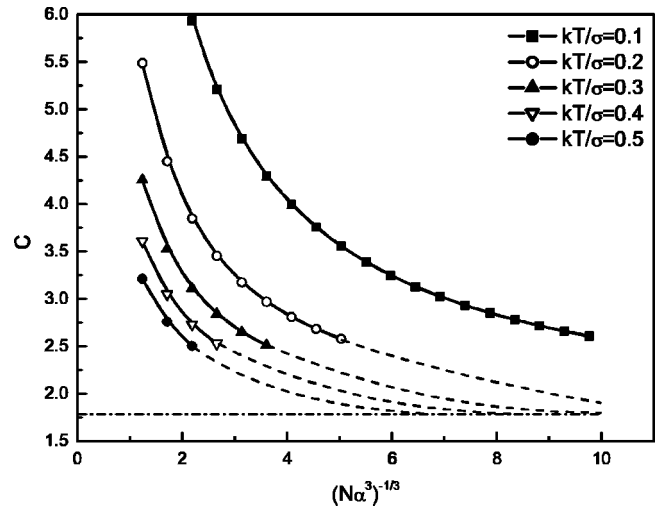
$C = 2$ and on the other hand by using the VRH theory described in Sec. II. One could argue that the corrections for α with respect to the magnitudes obtained from the simplistic theory are rather small and therefore the use of a more complicated theory for the evaluation α is unnecessary. However, it is seen in Table I that the following puzzle arises in the simplistic approach. For the hopping transport of holes in dispersions of N-isopropyl carbazole (NIPK) in polycarbonate (PVK), studied in Ref. 7, the simplistic approach with $p = 1/3$ and $C = 2$ gives widely different α values for different NIPK concentrations and, moreover, it yields different α values for different temperatures for a constant NIPK concentration. It is difficult to justify such kind of α dependences. On the other hand, the theory given in this report leads to very consistent estimates for α at all studied NIPK concentrations and temperatures. Therefore, we claim that if

TABLE I. Results for the decay length α of a carrier wave function in organic semiconductors extracted from experimental data for the low-field mobility vs the concentration of localized states, N.

Material	Carrier [a]	$N^{-1/3}$ (Å)	T (K)	$\tilde{C}$ (Å^{-1})	α (Å) [b]	α (Å) [c]	Reference
TNF/PVK [d]	e	8 . . . 15	295	1.1	1.8	3.0	5
TNF/PVK [d]	e	8 . . . 15	295	1.1	1.8	3.0	8
TNF/PVK	h	6 . . . 10	295	1.8	1.1	1.5	5
TNF/PVK [e]	e	7 . . . 8	295	2.2	0.9	1.2	5
NIPK/PVK	h	5 . . . 15	295	1.2	1.7	2.5	7
NIPK/PVK	h	10 . . . 18	363	1.0	2.0	2.5	7
NIPK/PVK	h	15 . . . 25	413	0.7	2.9	2.5	7
PVK/TPD	h	11 . . . 25	295	0.7	2.9	3.0	9
TPD/PC	h	9 . . . 17	295	1.8	1.1	1.0	9
TNF/PE	e	7 . . . 8	295	2.5	0.8	1.0	8

[a]Symbols "h" and "e" correspond to holes and electrons, respectively.
[b]Estimated assuming $C = 2.0$.
[c]Estimated using the slope factor $C(N\alpha^3, kT/\sigma)$ from Eq. (9).
[d]Electron transfer via complex TNF molecules.
[e]Electron transfer via free TNF molecules.

one fits experimental data by Eq. (1) with $p = 1/3$, which is possible in a restricted range of $N\alpha^3$, one should take into account the correct value for the slope parameter C from Fig. 4. This is particularly important for diagnostics of the decay length α of the charge-carrier wave functions in the localized states.

The concentration dependence of the hopping mobility of charge carriers in a random system of sites with a Gaussian DOS was recently studied by Arkhipov *et al.*[19] The results were presented in the form of Eq. (1) with C values less than 1.1 for very broad parameter ranges $0.11 \leq kT/\sigma \leq 0.32$ and $2.5 \leq (N\alpha^3)^{-1/3} \leq 50$. Related to these data we would like to make the following remark. Arkhipov *et al.*[19] report $C = 1.056$ for $kT/\sigma \approx 0.32$ and $(N\alpha^3)^{-1/3}$ close to 50. For such parameters, the strong inequality $(N\alpha^3)^{-1/3} \gg \sigma/kT$ is obviously fulfilled and one should expect the classical NNH result with $C \approx 1.73$ instead of $C = 1.056$ from Ref. 19. Therefore we cannot consider the results of Ref. 19 as being reliable due to their drastic deviation from the percolation result in the limiting case $(N\alpha^3)^{-1/3} \gg \sigma/kT$.

IV. CONCLUSIONS

A theory for the dependence of the charge-carrier mobility μ in the hopping regime on the concentration of localized states N is suggested for disordered organic solids. This dependence is known to be extremely pronounced leading to a mobility that varies by more than seven orders of magnitude due to a slight change in the concentration of localized states.[5,7–9] It is this dramatic effect that makes the subject so interesting and important. Our theoretical approach based on the concept of the transport energy yields, Eq. (9), for the dependence $\mu(N)$. The solution of this equation agrees with the results of computer simulations[14] and with experimental data.[8] It can be approximately presented in the form of Eq. (1) with parameters p and C given in Fig. 1 or in the form of Eq. (1) with $p = 1/3$ and C values given in Fig. 4. The results of the theory allow one to determine consistently the decay length α of the carrier wave function from the experimental dependence $\mu(N)$.

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