Concentration dependence of the hopping mobility in disordered organic solids

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Traditionally the dependance of the drift mobility, μ, on the concentration of localized states, N, in disordered organic solids is plotted in the form $\mu \propto \exp[-C(N\alpha^3)^{-p}]$ with $p = 1/3$ and constant C. This representation cannot be correct, because transport in disordered organic solids is essentially a variable-range-hopping process with a weaker dependence $\mu(N)$. We study this dependence theoretically and show that both parameters p and C strongly depend on temperature and hence they are not universal. Only at very high temperatures the formula with $p = 1/3$ is valid. The result is significant in particular for a correct diagnostics of the localization length α from the measured dependence $\mu(N)$.

1 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, 2, 3]. Transport properties of charge carriers attract most attention of the researchers. Correspondingly, the most studied physical quantity is the drift mobility, μ, of charge carriers. It has already become a tradition in the field of organic solids to represent the dependence of the drift mobility μ on the concentration of localized states N in the form

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

with constant C and $p = 1/3$ [4, 5, 6]. In this formula α is the localization length of carriers in the localized states. This representation, however, cannot be correct, because the hopping drift mobility in organic disordered solids evidences also a strong temperature dependence and hence the transport process is essentially a variable-range-hopping process (VRH). While the dependence described by Eq. (1) with constant C and $p = 1/3$ should be expected for the nearest-neighbour hopping (NNH) [7], the VRH should demonstrate a weaker concentration dependence and furthermore the exponent should also depend on temperature leading in the form of Eq. (1) to the temperature-dependent coefficient C. For example, in the case of a uniform energy distribution of localized states the concentration dependence of the the drift mobility is described by the famous Mott's law with $p = 1/4$ and $C \propto T^{-1/4}$ [7, 8].

Straightforward computer simulations have shown that the experimentally observed temperature dependence of the drift mobility [3], $\mu \propto \exp[-(T_0/T)^2]$, evidences the energy distribution of localized states

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(DOS) in organic disordered media to be Gaussian [2]:

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

Here σ is the characteristic scale of the energy distribution.

It is our aim in this report to obtain the concentration dependence of the drift mobility for the VRH transport of charge carriers via localized states with a Gaussian energy distribution and a random spatial distribution. Using the theoretical approach based on the concept of the transport energy [9] we show below that, as expected for the VRH process, the dependence $\mu(N)$ is weaker than $\ln(\mu) \propto N^{-1/3}$ and, more important, it essentially depends on temperature. Eq. (1) with $p \approx 1/3$ appears only approximately valid for high temperatures and/or for extremely low concentrations of localized states.

2 Theory

The jump rate of a carrier from an occupied localized state i to an empty localized state j is a product of a prefactor ν_0, a carrier wave-function overlap factor, and a Boltzman factor for jumps upward in energy [10]:

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{\alpha}\right) \exp\left(-\frac{\epsilon_j - \epsilon_i + |\epsilon_j - \epsilon_i|}{2kT}\right). \tag{3}$$

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 the Boltzmann constant. The most appropriate way to calculate the drift mobility μ of charge carriers in a disordered system with an exponentially broad distribution of local transition probabilities given by Eq. (3) is to average the inverse hopping rates over the real transitions performed by a mobile charge carrier [9]. Hence the carrier drift mobility can be evaluated as

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

where e denotes the elementary charge, $\langle t \rangle$ is the average hopping time and $R(\epsilon_t)$ is the typical length of hopping transitions to the transport energy, ϵ_t, from lower energy states determined by the concentration of localized states below ϵ_t. Neglecting the concentration dependence of the prefactor $(e/kT)R^2(\epsilon_t)$ in Eq. (4) compared to the exponential term in $\langle t \rangle$ one obtains for the drift mobility

$$\ln\left\{\mu/[eR^2(\epsilon_t)/kT]\right\} = -2\left[\frac{4\sqrt{\pi}}{3B}N\alpha^3\int_{-\infty}^{x_t/\sqrt{2}}\exp(-t^2)\,dt\right]^{-1/3} - \frac{x_t}{kT/\sigma} - \frac{1}{2(kT/\sigma)^2}. \tag{5}$$

The numerical coefficient $B = 2.7$ is introduced into Eq. (5) in order to warrant the existence of an infinite percolation path over the states with energies below ϵ_t. The transport energy as the function of the temperature and the concentration is evaluated as a solution of the equation [9]

$$\exp\left(\frac{x^2}{2}\right)\left[\int_{-\infty}^{x/\sqrt{2}}\exp(-t^2)\,dt\right]^{4/3} = \frac{kT}{\sigma}\left(9\sqrt{2\pi}N\alpha^3\right)^{-1/3}. \tag{6}$$

It is Eq. (5) that determines the dependence of the carrier drift mobility on parameters kT/σ and $N\alpha^3$. From the above equations it is clear that only these two parameters are essential for the results.

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. (5) does not provide a pure power law for the dependence of $\ln(\mu)$ on $N\alpha^3$,
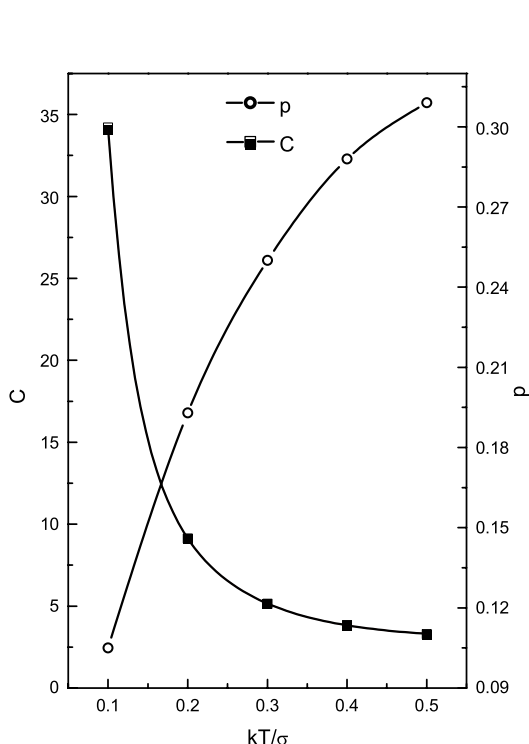
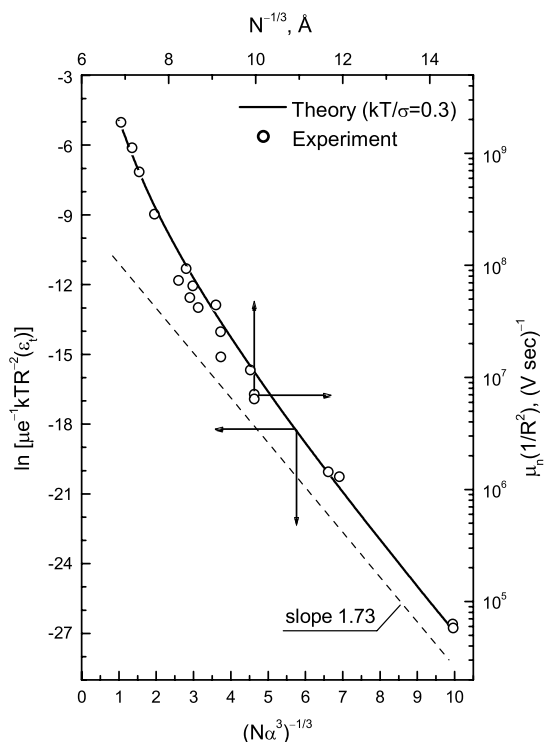**Fig. 1** Temperature dependence of the parameters C and p in Eq. (1).

Fig. 2 Concentration dependence of the drift mobility evaluated from Eq. (5) for $kT/\sigma = 0.3$ and observed in experiment [4].

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 ranges from 0.065 to 0.150 eV depending on the kind of dopant, dopant concentration, and host polymers [2, 3]. The temperature ranges in the experimental studies from 200 K to 350 K [3]. Hence the values of the parameter kT/σ in real experiments 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. (5) 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 essentially 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. (3) [7, 8]. Energy dependent terms in Eq. (3) 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 of charge carriers. The values of p in Fig. 1 obtained for a Gaussian DOS differ from the value $p = 1/4$ in the Mott's law valid for a constant, energy-independent DOS. With rising temperature, the value of p increases and it becomes close to $1/3$ at $kT/\sigma \approx 0.5$. For higher temperatures one should expect the validity of the nearest-neighbour hopping regime with $p \approx 1/3$. 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.

3 Discussion

The 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 $\ln[\mu e^{-1} kT R^{-2}(\epsilon_t)]$, obtained by solving Eq. (5), and experimental data for the drift mobility in TNF/PVK [4] 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. However, it is possible in a restricted concentration range and it has been done so far in all interpretations of experimental data in organic disordered media [4, 5]. One of the consequences of such plots was the apparent dependence of the localization length α on the concentration of impurities N [4, 5]. Our theoretical results in Fig. 2 demonstrate the same curvature of the $\ln[\mu e^{-1} kT R^{-2}(\epsilon_t)]$ versus $(N\alpha^3)^{-1/3}$ plots as the experimental data and they provide the fit for experimental data with a constant localization length α.

A strong temperature dependence of the slope parameter C, which is well seen in Fig. 1, evidences that the expression for the drift mobility μ cannot be factorized as $\mu(kT/\sigma, N\alpha^3) = \mu_0 \chi(kT/\sigma)\varphi(N\alpha^3)$. This is the essence of the VRH transport mechanism and it is in contrary to numerous statements in the scientific literature, which claim such a factorization possible (see, for example, [6]). Such a factorization is approximately possible only in the extreme case corresponding to the strong inequality $(N\alpha^3)^{-1/3} \gg \sigma/kT$ [7]. In such a case energy dependent terms in Eq. (3) (of the order σ/kT) do not contribute much to the jump probability compared to the spatially dependent terms (of the order $(N\alpha^3)^{-1/3}$). Under such circumstances the transport path of charge carriers is determined solely by geometrical factors. Such transport mechanism is known as the nearest-neighbor hopping. The drift mobility in the NNH is at best described by the percolation theory [7] and it is given by Eq. (1) with $p = 1/3$ and $C \approx 1.73$ [7]. Indeed a slope coefficient of our theoretical curve in Fig. 2 is very close to 1.73 for the limit of low concentrations $N\alpha^3$.

4 Conclusions

A theory for the dependence of charge carrier drift mobility in the hopping regime on the concentration of localized states is suggested for disordered organic solids. Theoretical consideration in the framework of a consistent concept of the transport energy in application to the VRH transport gives the dependence $\mu(N)$ in the form of Eq. (5). The solution of this equation can be approximately represented in the form of Eq. (1) with parameters p and C given in Fig. 1. The results of the theory agree with experimental data better than those of the simplistic approach with $p = 1/3$ and constant C.

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