How to Find Out the Density of States in Disordered Organic Semiconductors

J. O. Oelerich, D. Huemmer, and S. D. Baranovskii
Department of Physics and Material Sciences Center, Philipps-University, D-35032 Marburg, Germany

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We suggest a recipe on how to determine the density of states (DOS) in disordered organic semiconductors from the measured dependence of the charge carrier mobility on the concentration of carriers n. The recipe is based on a theory for the concentration-dependent mobility. As an example, we apply our theoretical results to experimental data obtained on two polymers and show that from the class of trial DOS functions $g(\varepsilon) \propto \exp\{-(\varepsilon/\sigma)^p\}$, only those with $p > 1.8$ can explain the experimental results. In particular, we claim that the concentration-independent mobility at low n evidences that the DOS cannot be purely exponential, which is in contrast to numerous recent assumptions in the literature.

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Charge transport and optical properties of organic disordered semiconductors, such as conjugated and molecularly doped polymers, are extensively studied due to applications of such materials in light-emitting diodes, field-effect transistors, and xerographic and photovoltaic devices [1–6]. The key feature of the material determining the optoelectronic properties is its energy spectrum, also called the density of states (DOS). Reliable first-principles calculations of the DOS in disordered organics are not yet known. Therefore, the only way to determine the DOS is to compare experimental data with the appropriate theory using some trial DOS functions $g(\varepsilon)$ aiming at the best agreement between experimental and theoretical results. At the first stages of research on organic semiconductors, it has been recognized in time-of-flight studies that the DOS in such systems is close to a Gaussian one, $g(\varepsilon) \propto \exp\{-(\varepsilon/\sigma)^2\}$ [7]. However in numerous later theoretical studies, a purely exponential form of the DOS, $g(\varepsilon) \propto \exp\{-(\varepsilon/\sigma)\}$, has been assumed [8–12]. In this Letter, we show how to reveal the DOS by studying the dependence of the charge carrier mobility μ on the concentration of carriers n. We apply our recipe to experimental data obtained on two widely studied polymers, PPV and P3HT [13,14], and show that the DOS in these organic materials is not purely exponential, but is instead close to a Gaussian one. Using this recipe, one can analyze the DOS in other organic materials by measuring the dependence of the mobility on carrier concentration.

In disordered organic systems, charge transport occurs via incoherent hopping of carriers (electrons or holes) between strongly localized states [1–8,10,11,15]. We assume that the energies of localized states are distributed via a DOS of the form

$$g(\varepsilon) = \frac{N}{C}\exp\left[-\left(\frac{\varepsilon}{\sigma}\right)^p\right], \qquad p > 0, \tag{1}$$

where N is the total concentration of localized states and σ is the energy scale of the order of ~ 0.1 eV [1–7,13–15]. Energy ε in Eq. (1) is counted positively downwards from some reference level $\varepsilon = 0$. Only the range of energies $\varepsilon \geq 0$ is considered, since the temperature T and the concentration of carriers n in experimental studies are low enough so that all important physics happens in the low energy part of the DOS. The normalization condition

$$\int_0^\infty g(\varepsilon)d\varepsilon = N \tag{2}$$

demands $C = \sigma\Gamma(p^{-1} + 1)$.

The hopping transition rate for a charge carrier from an occupied state i to an empty state j over a distance r_{ij} is described by the Miller-Abrahams expression

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{a}\right)\exp\left(-\frac{\varepsilon_i - \varepsilon_j + |\varepsilon_i - \varepsilon_j|}{2kT}\right), \tag{3}$$

where a is the localization length, which is assumed equal for sites i and j, and the preexponential factor $\nu_0 \simeq 10^{12}\ \mathrm{s}^{-1}$ depends on the interaction mechanism that causes transitions [1–6,16]. In the case of thermal equilibrium, which we consider, the energy distribution of carriers is described by the Fermi function $f(\varepsilon, \varepsilon_F) = \{1 + \exp[(\varepsilon_F - \varepsilon)/kT]\}^{-1}$ with the Fermi level ε_F determined by the condition

$$\int_0^\infty f(\varepsilon, \varepsilon_F)g(\varepsilon)d\varepsilon = n, \tag{4}$$

where n is the concentration of charge carriers. Equations (1)–(4) formulate a self-consistent theoretical model with three dimensionless parameters: σ/kT, Na^3, and n/N. Note that experiments are usually carried out at room temperature, so that $kT < \sigma$.

It is well known that in inorganic disordered semiconductors like a-Si:H or chalcogenides with purely exponential DOS given by Eq. (1) with $p = 1$ and $C = \sigma$, charge carriers dive in energy unlimitedly in course of time in an empty system at $kT < \sigma$ [3,17]. The speed of spatial charge carrier motion slows down and the transport coefficients appear time dependent. This regime is called dispersive transport. During dispersive transport, the carrier mobility μ always depends on the concentration of carriers n, since the diving in energy stops only when the energy position of carriers arrives at the vicinity of the n-dependent Fermi level $\varepsilon_F(n)$ and hence cannot dive further on [18,19].

Remarkably, it has been established experimentally for the most widely studied organic disordered materials, OCC-PPV and P3HT, that the carrier mobility being strongly n-dependent at large n, as typical also for inorganic materials, becomes independent on n at low concentrations [13,14]. This observation by itself excludes the possibility of the purely exponential DOS given by Eq. (1) with $p = 1$, since for $p = 1$ the equilibrium mobility is always determined by the position of the concentration-dependent Fermi level $\varepsilon_F(n)$ [3]. Therefore, it is not correct to approximate the Gaussian DOS by an exponential one, particularly in the regime of low carrier concentrations n. In the Gaussian DOS, the carrier mobility does not depend on n at low concentrations (see below), while in the exponential DOS the mobility is always dependent on n.

The reason for the n-independent mobility at low n is the following [20,21]: for DOS functions given by Eq. (1) with $p > 1$ even at negligibly low carrier concentrations, charge carriers do not dive in energy unlimitedly in course of time, but instead spend most time in the vicinity of the so-called equilibrium energy ε_∞, determined as [7,20,21]

$$\varepsilon_\infty = \frac{\int_0^\infty \varepsilon g(\varepsilon)\exp(\varepsilon/kT)d\varepsilon}{\int_0^\infty g(\varepsilon)\exp(\varepsilon/kT)d\varepsilon}. \quad (5)$$

Of course, the time $\tau(\varepsilon) \propto \exp(\varepsilon/kT)$ that carriers spend at energy ε increases exponentially with ε, but the probability to find states with large ε (note, we count energies downward as positive) decreases with increasing ε proportional to the DOS $g(\varepsilon)$, i.e., at $p > 1$ steeper than the increase of $\tau(\varepsilon)$. It is the interplay between these two ε-dependencies in $\tau(\varepsilon)$ and $g(\varepsilon)$ that provides a finite value of the equilibrium energy ε_∞. This feature gives the carrier mobility a definite value even in the empty system when the Fermi level is below ε_∞ [20–23], i.e., $\varepsilon_F(n) > \varepsilon_\infty$. Mobility becomes n-dependent only at such high concentrations that $\varepsilon_F(n) \le \varepsilon_\infty$ [3,20,21,24,25]. The critical concentration n_c, above which mobility becomes dependent on the carrier concentration n, is thus determined by the condition [3,20,21,24]

$$\varepsilon_F(n_c) \approx \varepsilon_\infty. \quad (6)$$

Both quantities, $\varepsilon_F(n)$ and ε_∞, are sensitive to the value of p in Eq. (1). Therefore, Eq. (6) can be used to determine the DOS by comparing the theoretical result for n_c given by Eq. (6) with experimental data. The only two model parameters involved in this criterion are σ/kT and n/N.

Energy relaxation of carriers in the DOS described by Eq. (1) with $p \ge 1$ resembles the multiple–trapping mode with the mobility edge replaced by some particular energy level ε_t called the transport energy (TE) [26]. For parameters σ/kT and Na^3 typical for disordered organics, the position of the TE is close to the reference energy $\varepsilon = 0$ for $p = 1$ [26] and for $p = 2$ [19,27], suggesting that it is true for all values $1 \le p \le 2$. In fact, not only for $p = 1$ the dispersive transport can take place as described above. At values $p > 1$ this regime with a time-dependent mobility is to be observed though within the time scale $t < t_{\mathrm{rel}}$, where the relaxation time t_{rel} is the time necessary for carriers to be thermally activated from the energy ε_∞ to the TE [22], i.e., $t_{\mathrm{rel}} \approx \nu_0^{-1}\exp(\varepsilon_\infty/kT)\exp(2N^{-1/3}/a)$.

Let us first try to estimate the shape of the DOS, namely, the value of p in Eq. (1), by estimating the magnitude of t_{rel}, which should be smaller than the time scale of experiments observing a time-independent mobility. In Fig. 1 we show the product $g(\varepsilon)\exp(\varepsilon/kT)$ for various values of the DOS exponent p in Eq. (1). As discussed in Refs. [22,23], this product determines the average time spent by carriers at different energies during the conducting process. The maximum of each curve corresponds to the value of ε_∞ that determines the equilibrium carrier mobility at low carrier concentrations [3,20,22]. One can recognize in the figure that for values $p < 1.5$, the time necessary for the carrier activation from ε_∞ to the maximum of the DOS, where the transport takes place [19,26] $\tau(\varepsilon_\infty) = \nu_0^{-1}\exp(\varepsilon_\infty/kT) \times \exp(2N^{-1/3}/a)$ would be larger than $\nu_0^{-1}\exp(110)$. This time is too large for any realistic experimental situation at any reasonable choice of ν_0. Only this argument excludes p values in the DOS [Eq. (1)] smaller than 1.5.

Let us now estimate the shape of the DOS applying criterion [Eq. (6)] to the experimental data obtained for organic disordered materials in Refs. [13,14]. Calculating $\varepsilon_F(n)$ via Eq. (4) and ε_∞ via Eq. (5), we obtain from Eq. (6) the values of n_c/N plotted in Fig. 2 for different choices of the DOS energy scale σ in Eq. (1). Also, the experimental data for OCC-PPV and P3HT from

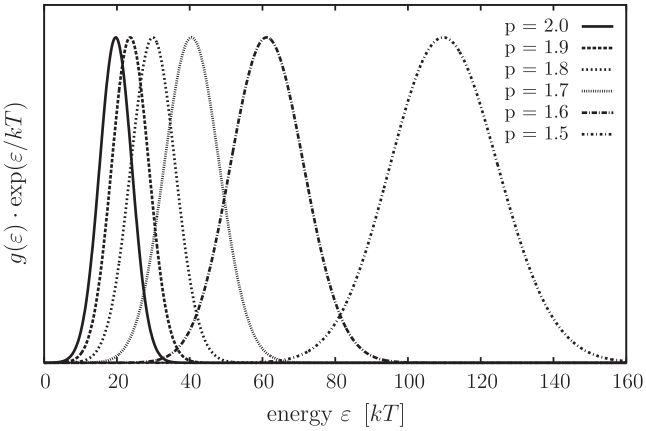

FIG. 1. The product $g(\varepsilon)\exp(\varepsilon/kT)$ as a function of energy for different DOS exponents p in Eq. (1) for $\sigma/kT = 4$. Energy is counted positively downwards from the reference point at the DOS maximum.

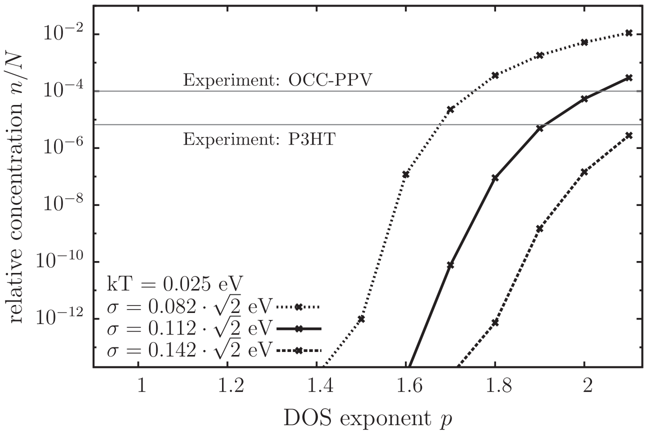

FIG. 2. The criterion of Eq. (6) is used to calculate the critical concentration n_c above which the Fermi level ε_F crosses ε_∞. n_c is plotted as a function of the DOS exponent p for different values of the energy scale σ of the DOS. The experimental results of Refs. [13,14] are shown as horizontal lines.

Refs. [13,14] are shown in the figure, for which we used $N = 3 \times 10^{20}$ cm^{-3} [13]. It is apparent from Fig. 2 that only p values in the range $1.7 < p < 2.2$ could describe the experimental data. As clearly seen, this conclusion is robust against increasing or decreasing the value of N by orders of magnitude and also against changing the energy scale of the DOS in a wide range. Therefore, one can conclude that the DOS in OCC-PPV and P3HT studied in Refs. [13,14] is close to a Gaussian one and is definitely not purely exponential.

So far we relied on the criterion in Eq. (6). Let us now calculate the charge carrier mobility μ and compare its n-dependence with the experimental data from Refs. [13,14]. We emphasize once again that for all DOS shapes given by Eq. (1) with $p \geq 1$ there is a particular energy level ε_t called the transport energy that has the following property: from energy levels below ε_t carriers perform hops to states in the vicinity of ε_t, while from the latter ones the carriers fall into energetically deeper spatially nearest states [22,26]. This hopping process near and below ε_t resembles a multiple-trapping-like process where ε_t plays the role of a mobility edge. Calculating the carrier mobility, one also has to take into account the percolation nature of hopping conduction, namely, that in order to provide an infinite percolation cluster of connected sites, one needs to take into account in average at least $B \simeq 2.7$ sites with highest rates available for any hopping event [23]. Literally extending the theory from Refs. [22,23] developed there for dilute systems to the case of finite concentration n, and using the theory from Ref. [19] for the transport energy ε_t, we obtain the following set of equations for the concentration-dependent mobility $\mu(n)$ in disordered semiconductors:

$$\mu = \frac{e}{kT} R^2(\varepsilon_t) \langle t \rangle^{-1}, \qquad (7)$$

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

$$\langle t \rangle = \nu_0^{-1} \frac{\int_{\varepsilon_t}^{\infty} \exp[\frac{2R(\varepsilon_t)}{a} + \frac{\varepsilon - \varepsilon_t}{kT}][1 - f(\varepsilon)] g(\varepsilon) d\varepsilon}{\int_{\varepsilon_t}^{\infty} g(\varepsilon)[1 - f(\varepsilon)] d\varepsilon}, \qquad (9)$$

where ε_t is determined by the equation

$$\frac{2}{3}\left(\frac{4\pi}{3B}\right)^{-1/3} \frac{kT}{a} \left[\int_{\varepsilon_t}^{\infty} [1 - f(\varepsilon, \varepsilon_F)] g(\varepsilon) d\varepsilon \right]^{-4/3} \times [1 - f(\varepsilon_t, \varepsilon_F)] g(\varepsilon_t) = 1. \qquad (10)$$

From Eqs. (7)–(9), one straightforwardly obtains the equation for the carrier mobility

$$\mu = \nu_0 \frac{e}{kT} \frac{3B}{4\pi R(\varepsilon_t) n_t} \exp\left(-\frac{2}{a} R(\varepsilon_t) - \frac{\varepsilon_F - \varepsilon_t}{kT} \right), \qquad (11)$$

with n_t determined as

$$n_t = \int_{\varepsilon_t}^{\infty} f(\varepsilon, \varepsilon_F) g(\varepsilon) d\varepsilon. \qquad (12)$$

Since the upward hops from the Fermi level ε_F to the TE ε_t dominate the charge transport, the carrier concentration below the TE, n_t, enters the set of equations. However, as mentioned above, for parameters σ/kT and Na^3 typical for disordered organics the position of the TE is close to the reference energy $\varepsilon = 0$ [19,27]. Hence, one can replace n_t by n in Eq. (11).

Using Eqs. (1), (2), (8), and (10)–(12), we calculate the mobility and obtain the data plotted in Fig. 3 for different values of the exponent p in Eq. (1). The critical concentrations observed experimentally in Refs. [13,14] are indicated in the figure as two vertical arrows. The parameters σ/kT and $N\alpha^3$ are chosen according to Refs. [13,14]: $\sigma = 0.112\sqrt{2}$ eV, $T = 293$ K, $N = 3 \times 10^{20}$ cm^{-3}, and

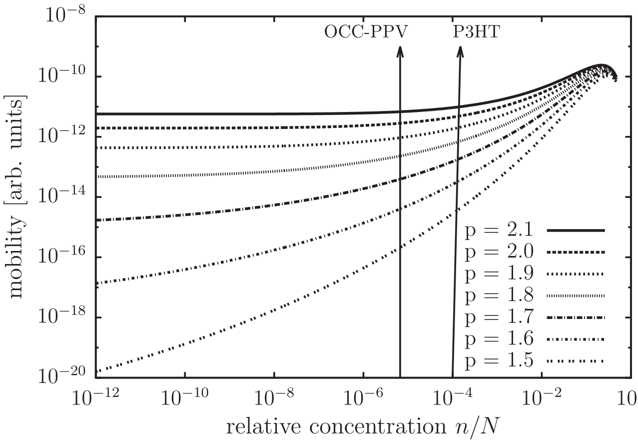

FIG. 3. Calculated mobility as a function of the relative charge carrier concentration n/N for different DOS exponents p in Eq. (1). The experimental results from Refs. [13,14] are indicated as vertical arrows.

$\alpha = 0.16$ nm. The result evidences again that DOS exponents of $p < 1.8$ in Eq. (1) cannot match the experimental data, since in the experiments mobility becomes independent of n at much higher values n_c [13,14] than a DOS with $p < 1.8$ would allow.

The dependence of the carrier mobility μ on the concentration n, although often highlighted, is in fact not surprising at all. Indeed the contribution of any pair of sites i and j to the hopping conductivity is proportional to the factor [3,16]

$$\nu_{ij} \propto \exp\left(-\frac{|\varepsilon_i - \varepsilon_j| + |\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F|}{2kT}\right). \quad (13)$$

It has the form of Eq. (3) only in the case if the starting site is occupied by the carrier and the target site is empty. Since the contribution of any pair of sites i and j depends on the carrier concentration n via the dependence of the Fermi energy on n in Eq. (13), it is not at all surprising that the mobility determined by hopping via localized states depends on n. However, what is remarkable is the independence of the mobility on n at concentrations below some critical value n_c, as it has been shown experimentally, for instance, in Refs. [13,14]. One can easily obtain this independence of μ on n for small concentrations n using the above general set of equations. In the low-concentration regime, the Boltzmann approximation for the Fermi distribution can be applied yielding

$$f(\varepsilon, \varepsilon_t) = [1 + e^{(\varepsilon_F - \varepsilon)/kT}]^{-1} \approx e^{-\varepsilon_F/kT} e^{\varepsilon/kT}. \quad (14)$$

In such a case, in accord with Eq. (12), $n_t \propto \exp(-\varepsilon_F/kT)$. Inserting this result for n_t into Eq. (11) cancels the concentration-dependent Fermi energy in this equation. Since the TE ε_t is independent of n at low concentrations [19], the expression for the mobility, Eq. (11), loses its n-dependence completely in the nondegenerate case, for which the Boltzmann approximation is valid. Note that this approximation is never valid for the purely exponential DOS of Eq. (1) with $p = 1$, while it is valid for a DOS with $p > 1$ in the case $\varepsilon_F > \varepsilon_\infty$ (note, we count energies downward as positive).

Our theoretical approach relies on the assumption that the DOS (i.e., the portion participating in transport) can be sufficiently well described by one set of trial functions. This might be well justified as long as there is no unfortunate superposition of inhomogeneously broadened, electronically inequivalent molecular states that may give rise to several "humps" in the DOS. Particularly, such a DOS structure with several peaks in the upper energy part of the DOS has been reported for several organic semiconductors on the basis of experimental studies using the Kelvin probe force microscopy and the gate-modulated activation energy spectroscopy [28–34]. Remarkably, in all these studies an exponential low-energy tail in the DOS has been reported. It would be very interesting to check this result by our method, namely by measuring the concentration dependence of the carrier mobility at low carrier concentrations, at which the low-energy tail dominates the charge transport. If a concentration-independent mobility is observed even at very low concentrations, one should check the validity of the experimental methods or revise the so far generally accepted transport model used in our Letter.

We conclude that by analyzing only the critical charge carrier concentration n_c below which the mobility becomes independent of the carrier concentration, one can determine the shape of the DOS in the systems, for which the DOS can be described by one set of trial functions.

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