Hopping charge transport in disordered organic materials: where is the disorder?

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Abstract

Effect of energetic disorder on charge carrier transport in organic materials has been reexamined. A reliable method for mobility calculation and subsequent evaluation of relevant disorder parameters has been discussed. This method is well suited for a direct calculation of the magnitude of dipolar disorder $\sigma_{\text{dip}}$ in polar organic materials from the current transients. Calculation of $\sigma_{\text{dip}}$ for several transport materials with varying concentration of polar dopants gives concentration dependences that are in reasonable agreement with theoretical predictions. A possible solution of the puzzle concerning the disorder effect on the mobility temperature dependence has been suggested.

Keywords: electron transport, drift mobility, energetic disorder

1 Introduction

Modern paradigm of the hopping charge transport in disordered organic materials (molecularly doped polymers, low-molecular weight organic glasses, amorphous polymers) states that the most important factor governing the behavior of a charge carrier is energetic disorder [1, 2]. It is generally accepted that hopping of a charge carrier in random energy landscape $U(\vec{r})$ describes very well all major features observed in transport experiments. Crucial ingredients of the most successful realization of this idea includes the Gaussian density of localized transport states

$$g(U) = \frac{N_0}{(2\pi\sigma^2)^{1/2}} \exp \left( -\frac{U^2}{2\sigma^2} \right), \quad (1)$$
and Miller-Abraham hopping rate \[3\]; here \(N_0\) is a total concentration of transport sites and \(\sigma\) is rms disorder. If we assume no spatial correlation between energies of different transport sites (a famous Gaussian Disorder Model (GDM) \[1\]), then the field and temperature dependence of the carrier drift mobility \(\mu\) could be described as \[1\]

\[ \mu = \mu_0 \exp \left( -2\alpha a \right) \exp \left[ -\frac{4}{9} \hat{\sigma}^2 + C \left( \hat{\sigma}^2 - \Sigma^2 \right) \sqrt{E} \right], \quad \hat{\sigma} = \sigma \beta, \quad \beta = 1/kT, \quad (2) \]

where \(a\) is a lattice scale for the equivalent homogeneous lattice model with the same concentration of transport sites (\(a\) scales as \(c^{-1/3}\) with concentration \(c\) of transport sites), \(\alpha\) is an inverse localization radius of the wave function of the transport level, parameter \(C\) scales as \(a\) and parameter \(\Sigma\) describes the positional disorder (more precisely, if \(\Sigma < 1.5\), then the term \(\Sigma^2\) in eq \(2\) should be replaced by 2.25).

In fact, the Poole-Frenkel (PF) mobility field dependence \(\ln \mu \propto \sqrt{E}\), usually observed in experiments, could be described by the GDM only in rather narrow field range around \(E \approx 1 \times 10^6\) V/cm. This limitation was naturally removed in the more advanced model of correlated disorder \[4, 5, 6, 7\]. Indeed, one of the basic assumptions of the GDM, i.e. the assumption of the absence of spatial correlations in the random energy landscape proves to be spectacularly wrong in organic materials. In these materials interaction of a charge carrier with randomly located and oriented dipoles (the model of dipolar glass \[4\]) or quadrupoles (the model of quadrupolar glass \[8\]) generates highly correlated energy landscape with correlation function \(C(r) = \langle U(\mathbf{r})U(0) \rangle\) decaying as \(1/r\) for the dipolar glass \[4, 6\] and as \(1/r^3\) for the quadrupolar glass \[8\]. The model of dipolar glass (DG) is a good candidate to describe transport properties of polar disordered organic materials, while the model of quadrupolar glass (QG) naturally describes non-polar materials having zero dipolar moment but nonzero quadrupolar moment; quadrupolar moments are sufficiently high for transport molecules having local polar groups with compensating dipolar moments \[8\].

Correlated landscape in the dipolar glass naturally produces the Poole-Frenkel mobility field dependence, as it was shown in one dimensional (1D) model of charge transport, where correlation function with power-law decay \(C(r) \propto 1/r^n\) leads to the mobility field dependence \(\ln \mu \propto E^{n/(n+1)}\) \[6\]. This conclusion has been confirmed by the 3D Monte Carlo simulation \[7\], where the mobility obeys the relation

\[ \mu = \mu_0 \exp \left( -2\alpha a \right) \exp \left[ -\frac{9}{25} \hat{\sigma}^2 + C \left( \hat{\sigma}^{3/2} - \Gamma \right) \sqrt{eaE/\sigma} \right], \quad (3) \]

with \(C \approx 0.78\) and \(\Gamma \approx 2\) for the case of totally filled lattice. In striking contrast with the GDM, the model of dipolar glass (sometimes called the correlated disorder model) demon-
strates the Poole-Frenkel field dependence in the field range from $10^4$ V/cm to $10^6$ V/cm, in good agreement with experimental data. For nonpolar materials the QG model gives $\ln \mu \propto E^{3/4}$, but this dependence is hardly distinguishable from the PF dependence in rather narrow field range typical for time-of-flight (TOF) data in nonpolar materials [9, 10, 11].

Recent paper by Schein and Tyutnev [12] put forward a challenge to this picture. They analyzed a vast set of data on the temperature dependence of the mobility, extrapolated to the zero electric field (in short, mobility temperature dependence). According to eqs 2 and 3, $\ln \mu(E \to 0) \propto -\hat{\sigma}^2$, giving us an obvious opportunity to calculate $\sigma$ from the TOF data. If we assume that different sources of energetic disorder are independent, then the total $\sigma^2$ is a sum of contributions from the individual sources

$$\sigma^2 = \sum_i \sigma_i^2. \tag{4}$$

One of the most important sources of energetic disorder in polar organic materials is a dipolar disorder, properly described by the DG model. For a lattice version of the DG model on a simple cubic lattice

$$\sigma_{dip}^2 = 5.53 \frac{e^2 p^2 c}{\varepsilon^2 a^4}, \tag{5}$$

here $c$ is a fraction of sites, occupied by dipoles, $p$ is a dipole moment, and $\varepsilon$ is a dielectric constant of the medium [13, 14].

We should expect that other sources provide contributions to the sum in eq 4, e.g. charge-quadrupolar interactions or van-der-Waals (charge-induced dipole) interactions. Nonetheless, if we consider highly polar transport dopants (with $p = 3 - 5$ D) in nonpolar polymer binder, e.g. polystyrene (PS), then we could reasonably expect that the dipolar term (eq 5) gives a dominant contribution to the total sum, so $\sigma$ should decrease with the decrease of the concentration of transport dopant $c$. Yet in [12] it was noted that experimental data demonstrate approximately constant magnitude of $\sigma$ for $c$ varying from $10\%$ to $70\%$. The only way to provide an agreement between eq 5 and experimental observations seems to suggest a contribution to eq 4 which increases with the decrease of $c$. Although such contributions do really exist (for example, charge-quadrupolar or van-der-Waals interactions of charge carrier with polystyrene units), their contributions are expected to be much smaller than the dominant dipolar contribution. According to the analysis of Schein and Tyutnev, the situation is very general. For this reason they concluded that the most possible reason for the mobility temperature dependence is a contribution from some intramolecular mechanism. A potential reader of their paper may ask an unavoidable question: where is the
disorder? Why does not it manifest itself in the temperature dependence of the mobility? In this paper we are going to discuss this fundamental problem affecting any possible disorder model of charge carrier transport in organic materials.

2 How to calculate $\sigma_{\text{dip}}$

In order to resolve a problem of the mysterious absence of the disorder effect, let us start with the examination of the crucial difference between the GDM and correlated models. We already noted that the PF behavior cannot be described in any convincing way by the GDM but arises naturally in the DG model. The most important transport property of the correlated disorder is a relation between the spatial decay of the correlation function and the mobility field dependence [6]. This fundamental relation offers a possibility to calculate a contribution from the dipolar disorder to the total $\sigma$ directly from the TOF data.

This can be done because according to the correlated disorder formalism (the simplest tool here is a 1D transport model developed in [6]) the most important contribution to the mobility field dependence for moderate field is provided by the most correlated component of the disorder, i.e. the component with the slowest decay of the correlation function $C(r)$. For example, for the algebraic correlation function $C(r) = A \sigma^2 (a/r)^n$ in the most important case of strong disorder $\sigma \beta \gg 1$ the 1D model gives

$$
\ln \mu/\mu_0 = G(T, E) \approx -2\alpha a - \sigma^2 \beta^2 + \left(1 + \frac{1}{n}\right) \sigma \beta (A \sigma \beta) \frac{1}{n+1} \left(\frac{eaE}{\sigma}\right)^{\frac{n}{n+1}}.
$$

As we already noted, $n = 1$ for the dipolar disorder and $n = 3$ for the quadrupolar disorder; in both cases a dimensionless constant $A \simeq 1$ [4, 8]. Formally, the GDM case may be considered as the limit $n \to \infty$. Mobility field dependence can be estimated by the derivative

$$
\frac{\partial G}{\partial E} = \frac{\sigma}{ea} (A \sigma \beta) \frac{1}{n+1} \left(\frac{\sigma}{eaE}\right)^{\frac{1}{n+1}}.
$$

Taking into account that $\sigma \beta \gg 1$ and $eaE/\sigma \leq 1$, we see that the right hand side in eq 7 decreases with the increase of $n$, i.e. with the decrease of the strength of spatial correlation (contribution of the multiplier $n^\frac{1}{n+1}$ is unimportant). Thus, eq 7 indicates that the most correlated disorder provides the most important contribution to the mobility field dependence.

Dominant role of the dipolar disorder could be easily demonstrated for the case of the two component disorder

$$
U(\vec{r}) = U_{\text{dip}}(\vec{r}) + U_n(\vec{r}),
$$

4
where some less correlated independent random energy $U_n(\vec{r})$ gives an additional contribution to the total disorder. If the correlation function for this contribution has a form $C_n(\vec{r}) = A_n \sigma_n^2 a_n^{2n}$ with $n > 1$, then the 1D model shows that at the low field boundary of the PF region $ea\beta E \gtrsim (\sigma_{\text{dip}}^2 \beta^2)^{-1}$ the additional contribution to the mobility field dependence is small, if

$$n \frac{\sigma_n^2}{\sigma_{\text{dip}}^2} \left( \beta^2 \sigma_{\text{dip}}^2 \right)^{n-1} \ll 1$$

(see Appendix). In many organic materials $\beta \sigma_{\text{dip}} \gg 1$ and dipolar contribution dominates the mobility field dependence even if $\sigma_n \simeq \sigma_{\text{dip}}$.

The result of the 1D model could be supported by the direct 3D Monte Carlo simulation of charge carrier transport in the energy landscape comprised by the mixture of the dipolar and non-correlated GDM disorder (see Figure 1). In Figure 1a the decrease of the slope $S = \frac{\partial G}{\partial E_{1/2}}$ of the mobility field dependence (or decrease of $\frac{\partial G}{\partial E}$ in Figure 1b) for $eaE/\sigma \leq 1$ with the decrease of dipolar contribution $\sigma_{\text{dip}}$ to the total $\sigma$ is clearly visible.

**Figure 1:** Mobility field dependences for a mixture of dipolar and non-correlated GDM disorder for the constant value of the total $\sigma$; here $\mu_s = \mu_0 \exp(-2\alpha a)$, $\sigma^2 = \sigma_{\text{dip}}^2 + \sigma_{\text{GDM}}^2$, and the ratio $r = \sigma_{\text{dip}}^2/\sigma^2$ is indicated at the corresponding curve. Transients have been simulated for $kT/\sigma = 0.26$. If $a \approx 1$ nm and $\sigma \approx 0.1$ eV, then $eaE/\sigma \approx 1$ for $E = 1 \times 10^6$ V/cm. Note the transformation of the mobility field dependence for moderate field from the PF type for $r = 1$ to the linear dependence $\ln \mu \propto E$ for $r = 0$. This very dependence is an intrinsic property of the GDM [7].
Hence, the temperature dependence of the slope $S(T)$

$$S(T) = \frac{\partial G}{\partial E^{1/2}} = C \left( \hat{\sigma}^{3/2} - \Gamma \right) \sqrt{ea/\sigma}$$

in polar materials could be used for a direct evaluation of $\sigma_{\text{dip}}$. Other sources of disorder, as well as the contribution from traps [15], provide much less significant contributions to $S(T)$ for $eaE < \sigma_{\text{dip}}$. Situation is especially favorable for highly polar dopants in PS matrix because the dipolar moment of styrene molecule is only 0.4 D [16], and we can expect that the quadrupolar moment of styrene is rather low too (styrene molecule is built only by carbon and hydrogen atoms and does not contain polar groups). Traps do not affect $S(T)$, either [17]. In future we will use notations $\sigma_S$ for the rms disorder, calculated from $S(T)$, and $\sigma_T$ for the corresponding rms disorder, calculated from the temperature dependence of $\mu(E \to 0)$.

![Figure 2: Dependence of $\sigma$ on the concentration of polar constituents [18, 16]: $\sigma_S$ (empty symbols) and $\sigma_T$ (filled symbols), correspondingly. Squares correspond to the system DEH:PS [18], circles correspond to the system with copolymer PS-BA as a binder [16], and lines are shown as a guide for an eye. Data from the paper [19] are not shown to avoid overcrowding of the figure.](image)

Information we needed is pretty rare in literature and we found only four papers where the data for $S(T)$ have been provided for different concentrations of polar constituents [16, 18, 20, 19]. Fortunately, these papers describe very different situations. Two papers consider dependence of the mobility on the concentration of highly polar transport dopants
DEH (4-diethylaminobenzaldehyde diphenylhydrazone, \( p = 3.61 \) D) \[18\] and TPM-E (triphenylmethane derivative, \( p = 2.1 \) D) \[19\] in PS matrix. The third paper describes dependence of the mobility on the concentration of polar units in the copolymer of styrene with polar monomer BA (butylacrilate, \( p = 1.52 \) D) \[16\], serving as a polymer binder, and the last paper considers an effect of the inert polar dopant TAP (\( t \)-amylphthalonitrile, \( p = 6.6 \) D) \[20\] on the charge transport in weakly polar transport material. In the two last cases concentration of the transport dopant was fixed. In all cases calculated \( \sigma_{\text{dip}} \) demonstrates the same expected trend (see Figures 2 and 3): it decreases with the decrease of the concentration of polar constituents with the expected magnitude of the decrease (apart from the case of TPM-E:PS, where the decrease is rather small).

![Figure 3: Dependence of \( \sigma^2 \) on the concentration of inert polar dopant TAP \[20\]: \( \sigma^2_S \) (empty squares) and \( \sigma^2_I \) (filled squares), correspondingly. Lines are shown as a guide for an eye.](image)

It is worth noting the almost linear dependence of \( \sigma^2_S \) on \( c \) for the transport material with small concentration of polar dopant TAP, in good agreement with eq \[5\] (Figure 3). We should expect that the model of ideal dipolar glass without any orientational correlation between dipoles is best suited for a description of this very situation: low concentration of polar dopant in amorphous material. Concentration dependencies of \( \sigma_S \) in Figure 2 do not obey eq \[5\]. This deviation may reflect a partial orientational ordering of dipolar molecules for high concentration of dipoles or a defect of the particular method of the mobility calculation, discussed in detail in the next section.
We would like to emphasize that the very scarcity of the published data on the temperature dependence of $S$ could be considered as a strong argument in favor of general agreement between predictions of the correlated disorder model and experiment. Four papers [16, 18, 20, 19] may be regarded as four random picks chosen from the vast variety of the TOF data. Remarkably, these four random picks immediately demonstrate reasonable agreement with theoretical predictions.

If the dipole moments of all constituents of the transport layer are low, then the DG model is clearly inadequate for the description of the charge transport. The most promising candidate in that case is the QG model. Here we provide only a very brief summary of the Monte Carlo simulation results for the QG model, more complete report will be published elsewhere. General approach is almost identical to the one described in [7]. Results of the simulation (see Figure 4) could be summarized as

$$\mu = \mu_0 \exp(-2\alpha a) \exp\left[-0.37\tilde{\sigma}^2 + C_Q (\tilde{\sigma}^{5/4} - \Gamma_Q) \left(eaE/\sigma\right)^{3/4}\right],$$

with $C_Q = 0.87$ and $\Gamma_Q = 1.91$. In nonpolar organic materials mobility field curves should be fitted to eq 11 and the corresponding quadrupolar $\sigma$ should be estimated from the temperature dependence of the slope of the dependence $\ln \mu$ vs $E^{3/4}$.

### 3 Dangers of low field mobility

In the previous section it was demonstrated that dipolar energetic disorder in organic materials can be directly evaluated from the TOF data. Result of this evaluation demonstrates a reasonable behavior of $\sigma_{\text{dip}}$ with respect to concentration of polar constituents. Magnitude of $\sigma_{\text{dip}}$ (and its variation with concentration) again is in reasonable agreement with the theoretical estimation by eq 5. Now we can reformulate the crucial question raised in the Introduction in a different way: why does the energetic disorder manifest itself in the mobility field dependence, but not in the mobility temperature dependence? Why the difference?

Discussion in the previous section unambiguously demonstrates that disorder does affect hopping transport of charge carriers in organic materials. We cannot consider as a possible alternative explanation an assumption that some totally unknown mechanism is responsible for the PF field dependence and, at the same time, it just by accident provides the same dependence of transport parameters on the concentration of polar dopants as a well known mechanism of the correlated dipolar disorder.

If disorder does affect charge transport, then there is no possibility to avoid a corresponding term proportional to $\sigma_{\text{dip}}^2$ in the mobility temperature dependence. According to
Figure 4: Mobility field dependence in the QG model for different values of $kT/\sigma$ (from the top curve downward); straight lines indicate the fit for eq [11]. Plot of the simulation data in the usual PF presentation $\ln \mu$ vs $E^{1/2}$ demonstrates much stronger deviation from the linearity in the weak field region.

the estimations of eqs [5] and [3] this term is not negligible but quite comparable to the total $\sigma^2$. Hence, only two possibilities are feasible: either some compensating mechanism provides a contribution to the total $\sigma$ (more rigorously, to the slope of the mobility temperature dependence) or some defects of the experimental procedure masquerade the true dependence of $\sigma$ on $c$. Let us consider both possibilities.

### 3.1 Possible physical compensating mechanisms

In the previous sections we demonstrated that $S(T)$ gives a robust estimation for the magnitude of $\sigma_{\text{dip}}$. Temperature dependence of the low field mobility is not so easily tractable. A host of various contributions adds to the resultant dependence: charge-dipole, charge-quadrupole, van der Waals (charge-induced dipole) interactions, polaron contribution of a simple Arrhenius type [21], and the similar contribution from traps. Reliable separation of the individual contributions to the resultant temperature dependence is impossible. As it was already mentioned, some contributions could provide compensating effects, for example contributions originated from the carrier interactions with polymer binder, though the magnitude of the effect is expected to be insufficient for a total compensation in the case
of highly polar transport dopant in the PS binder. There is another possibility for compensation because for a low concentration of the dopant charge transport should become more sensitive to the energetic disorder: exponential decrease of the hopping rate for large average distances between dopant molecules results in carrier hopping to the nearest neighbor without regards to its energy. This means that the effective $\sigma_T$ should increase with the decrease of $c$, but this effect is hardly very important for $c > 10 - 15\%$.

Effect of impurities (possible traps) deserves a special discussion. First of all, traps do affect effective magnitude of $\sigma_T$, at least the one estimated using the GDM [22]. Effect of impurities could be responsible for different values of $\sigma_T$ observed for the same material. For example, dependence of $\sigma_T$ on $c$ for the same system DEH:PS was found to be different in different papers [18, 23]. In the earlier paper [23] a constant value $\sigma_T \approx 0.13$ eV was found. In the later paper [18] more rigorous purifying procedures were used and very careful preparation procedure was undertaken. As a result, variation $\approx 15\%$ in the magnitude of $\sigma_T$ over studied concentration range has been found (see the corresponding curve in Figure 2). This is certainly beyond the experimental error range. For the same concentration of DEH, magnitude of $\sigma_T$, reported in Refs. [18] and [23], differs up to 20-25%. This means that the slope of the mobility temperature dependence could differ up to 40% for different procedures of material purification and sample preparation. In [12] the result of [18] is mistakenly regarded as corroborating the conception of intramolecular origin of $\sigma_T$, while in fact comparison of the results of Refs. [18] and [23] suggests that more careful examination of the trap effect on $\sigma_T$, calculated from the TOF data, is needed.

Some details of the preparation procedure, exploited in [18], are unusual. For example, coating of the transport layer was performed under the red light to avoid photochemical creation of traps. Quite probably, this very careful preparation procedure gave a possibility to avoid excessive amount of traps and obtain more reliable values of $\sigma_T$.

Note, that polymers are difficult to purify; to some extent, all of them contain various impurities, possibly serving as traps. Analysis of charge transport in trap-containing materials shows that increase in trap concentration could be interpreted as an increase of the effective $\sigma_T$ [24]. In molecularly doped polymers decrease of the dopant concentration means a simultaneous increase of the polymer concentration and, thus, possible increase in concentration of traps. This could provide an additional compensating mechanism.

### 3.2 Deficiency of the mobility calculation

So far we considered a possible compensation that is relayed to some intrinsic physical mechanism. Yet, quite probably, the most important reason for the compensation is a
peculiar procedure for the calculation of the drift mobility, employed in the majority of experimental papers.

There are two most frequently used procedures for the calculation of $\mu = L/Et$ from the TOF data in double linear current vs time presentation: 1) calculation that uses time $t_i$ determined by the intersection of asymptotes to the plateau and trailing edge of the transient and 2) calculation that uses time $t_{1/2}$ for current to reach half of its plateau value; here $L$ is a thickness of the transport layer. The first method is a method of choice for most papers. One can find in literature the statement that the difference between two procedures is not very important for determination of the temperature and field dependence of the mobility \cite{25, 26}. This is not true.

![Figure 5: Mobility field dependence for two methods of the mobility calculation: $\mu_i$ (filled squares) and $\mu_{1/2}$ (empty squares) \cite{27}. Straight lines indicate best fits.](image)

Calculation, based on $t_i$, significantly overestimates contribution of fast carriers. Deficiency of this calculation is especially evident in the case of materials with traps. In trap-free materials the use of $\mu_i$ leads only to the change of the slope of the mobility field dependence. In the presence of traps the use of $\mu_i$ sometimes distorts even the functional type of the mobility field dependence, bringing it to the linear one $\ln \mu_i \propto E$. This behavior was observed in experiment \cite{28}, but it is an artifact, directly related to the inferior method of the mobility calculation \cite{29}. Procedure that uses $t_{1/2}$ is much more reliable and generally agrees well with the standard definition of the mobility as $\mu = v/E$, where $v$ is an average carrier
velocity.

Unfortunately, errors, related to the use of $t_i$, are not limited to the mobility field dependence, they also affect the mobility temperature dependence. As an illustration we provide Figure 5, where the temperature dependence of $\mu_i$ and $\mu_{1/2}$ for tri-$p$-tolylamine doped polystyrene [27] is shown. Slopes of the dependencies differ by approximately 20%, thus the values of $\sigma_T$, calculated from the slopes, do differ too. Similar difference was found for the data presented in [30]. Again, as in the case of the temperature dependence of $S$, the data for raw transients (note that here we need transients for several values of $T$) is very difficult to find in literature.

It is very important to understand the full significance of the described fact. If we calculate $\sigma_T$ from the slope of the mobility temperature dependence for different values of $c$ and use the mobility $\mu_i$, then there is absolutely no guarantee that its relative difference from the value of $\sigma_T$, calculated from $\mu_{1/2}$, remains constant in the whole range of concentration. Remember, $\mu_{1/2}$ is a much better approximation for a true mobility. Hence, the obtained concentration dependence of $\sigma_T$ is certainly not very reliable and, quite probably, has considerable errors.

### 3.3 Non-dispersive or dispersive transport?

There is another aspect of the mobility calculation procedure that can be a possible source of errors. It was claimed in [12] that for all cases used in the analysis of charge transport, transport regimes are essentially non-dispersive. This is not true. For example, Borsenberger et al. explicitly emphasized that transients for highly polar dopant DTNA (di-$p$-tolyl-$p$-nitrophenilamine, $p = 5.78$ D) in PS are highly dispersive and no plateau was observed in the whole field, temperature and concentration range; sometimes the transit time has been even determined by the intersection of the asymptotes in double logarithmic current vs time representation [31]. For this very reason $\sigma_T$ was even calculated by the formula

$$\ln \mu/\mu_0 \approx -2\alpha a - \frac{1}{4} \hat{\sigma}^2$$

(12)

that differs from eq [2] It was suggested by Bässler and Borsenberger [32] for the treatment of low field mobility in the case of dispersive transport. Particular material DTNA:PS could be an exceptional case in the sense that in the whole range of all relevant parameters $c$, $T$, and $E$ transients demonstrate no visible plateau, but for low temperature ($T \leq 230$ K) this kind of transients is generally a rule and not an exception [32] [33] [34]: how the transit time $t_i$ (or $t_{1/2}$) could be reliably calculated in double linear plot is not very clear in this situation.

In fact, sometimes the problem of the choice between non-dispersive and dispersive trans-
port regime is even more tricky than described in the previous paragraph. For example, let us consider again the case of DTNA-doped PS. In the original paper [31] transients were considered as dispersive because no visible plateau was observed. Yet it is very well known that non-dispersive transport (described by the usual diffusion equation with well defined \( v \) and diffusion coefficient \( D \)) can routinely produce the same kind of transients if \( vL/D \leq 5 - 10 \). Such transients have no well defined plateau but could be easily discriminated from the true dispersive transients by their asymptotes for \( t \to \infty \). True dispersive transport transients obey the law \( I(t) \propto t^{-1-\alpha} \) [35], while for a normal diffusion \( I(t) \propto \exp(-v^2t/4D) \), putting aside an unimportant power-law factor.

This test immediately demonstrates that at least some transients, provided in [31], are not dispersive: the transient can be fitted with reasonable accuracy by the solution of the diffusion equation [36, 37, 38]

\[
I(t) \propto \sqrt{\frac{D}{\pi t}} \left[ \exp \left( -\frac{v^2t}{4D} \right) - \exp \left( -\frac{(L-vt)^2}{4Dt} \right) \right] + v \left[ \text{erf} \left( \frac{L-vt}{\sqrt{4Dt}} \right) + \text{erf} \left( \frac{vt}{\sqrt{4Dt}} \right) \right],
\]

(13)

where \( \text{erf}(x) \) is the error function, and the large time asymptotic is of the exponential kind (see Figure 6). We can safely conclude that in some cases charge transport in DTNA:PS occurs in the non-dispersive regime, and yet it was always analyzed using eq 12, suitable only for highly dispersive regime! All this confusion means that the true magnitude of \( \sigma_T \) and its dependence on \( c \) are very different from provided in [31]. One can learn a very important lesson from this example: in order to calculate mobility from transients without plateau the very first step should be an attempt to fit the transient to eq 13.

One can conclude that the data, discussed in [12], had been obtained both for non-dispersive and dispersive regimes. Even worse, in some cases a non-dispersive mobility had been treated as a dispersive one, leading to the patently wrong calculation of \( \sigma_T \). We believe that in this situation it is impossible to reveal the true dependence of the rms disorder on the concentration of polar constituents.

### 3.4 Possible hints for improper treatment of TOF data

Discussion of possible difficulties relevant to the analysis of TOF transients and evaluation of the disorder parameters from the TOF data should be finished with one additional remark. Although current transients are of primary importance for a detection of possible deficiencies of the mobility calculation procedure, sometimes the hints for the improper treatment of the transport data could be obtained directly from \( \mu(E) \) or \( \mu(T) \) curves.

One very well known example is an artifact of the mobility decrease with the increase of
Figure 6: Transport transient from Figure 2 of [31] (crosses) and the best fit for eq 13 (line). Note that \( \ln I(t) \propto t \) for \( t \gg L/v \).

\( E \) in weak field region. Earlier this phenomenon was attributed to the effect of field induced traps [1], though this explanation for weak field region always looks pretty suspicious. Later it was found that the true reason for this strange behavior is a deficiency in the mobility calculation procedure, i.e. the use of \( \mu_i \) [36, 37, 39]. If fitting of the transients to eq 13 is used, then the mobility curve becomes monotonously increasing with \( E \). The reason for the unexpected increase of \( \mu \) in weak field region is a trivial contribution from the normal diffusion, described by the diffusion coefficient \( D \). It is worth noting that the fitting procedure, suggested by Hirao et al. [36, 37], produces an additional important result: it removes the spurious dependence of \( \mu \) on the thickness of the transport layer \( L \) (\( D \) was also found to be independent of \( L \)).

Artifact of the mobility field dependence in weak field is directly related to the main subject of our consideration. Mobility that decays with the increase of \( E \) was reported for transport material TAPC:PC (1,1-bis-(di-4-tolylaminophenyl)cyclohexane in polycarbonate) doped with small amounts of inert polar dopants o-, m-, and p-DNB (isomers of dinitrobenzene) [40]. For m-DNB and p-DNB the mobility decays with the increase of \( E \) in the whole field range (up to \( E \approx 1 \times 10^6 \) V/cm). Such behavior for room (or lower) temperature is extremely unusual and, very probably, indicates an improper method of the mobility calculation from the TOF data. Correspondingly, magnitude of \( \sigma_T \), provided in [40] and extensively
discussed by Schein and Tyutnev [12], is hardly very reliable.

Highly unusual value of some relevant parameter, obtained from the interpretation of TOF data, could serve as another alarm signal. As an example of such alarm signal we consider an unusual value of the radius of the localization $R_0$ of the wave function of transport site, obtained for DEH:PS [23]. It was found that $R_0 = 1/\alpha = 4.8 \text{ A}$, while for all other transport materials $R_0$ typically falls in the range $1 - 2.5 \text{ A}$ [41, 42, 43, 44]. We believe that this is another indication that something goes wrong with the mobility calculation; again, the use of $\mu_i$ is a probable culprit.

4 Checklist for the reliable mobility calculation and subsequent evaluation of the disorder parameters

In this section we would like to emphasize principal details of the more safe and reliable procedure for the analysis of the TOF data in order to elucidate disorder parameters.

- First of all, wherever possible, transport should be analyzed for a non-dispersive regime only. In this regime transport parameters are more sensitive for peculiarities of the random energy landscape (comparison of eqs 2 and 12 supports this statement for the GDM).

- If a well defined plateau of the transient is observed, then the drift mobility may be calculated using $t_{1/2}$. Use of $t_i$ should be completely eliminated from the experimental practice.

- If there is no well defined plateau, then the transient should be fitted to eq 13 according to the procedure, suggested by Hirao et al. [36]. Only in the case, when the quality of the fit is clearly inadequate, transport should be analyzed in the framework of the dispersive regime.

- For the case of dipolar disorder, $\sigma_{dip}$ should be calculated from the temperature dependence of the slope of the mobility field dependence $S(T) = \frac{\partial \ln \mu}{\partial \mu}$ for moderate field using eq 3. The use of the DG model instead of the GDM is important, because the very essence of this approach is based on the transport properties of correlated energy landscape. This method is almost completely insensitive to the contribution from traps, polaron effects, and van der Waals interaction. The quadrupolar contribution probably could not be totally eliminated in this way, but we may reasonably expect that it is not dominant for polar materials.
For nonpolar materials the magnitude of quadrupolar disorder should be calculated from the temperature dependence of the corresponding slope $S_Q(T) = \frac{\partial \ln \mu}{\partial E/4}$ according to eq[11]. Unfortunately, description of the mobility field and temperature dependence for real organic materials with contributions from different sources of disorder having different correlation properties cannot be described by any simple unified formula.

Discussion of the dependence of $\sigma_T$ on the concentration of dipolar dopants and other relevant parameters should be performed only after calculation of $\mu$ and $\sigma_S$ in the proper way. We hope that the realization of this program will provide us with much more reliable knowledge of the crucial parameters of the energy landscape in disordered organic materials.

5 Conclusion

This paper is a direct response to the recent review by Schein and Tyutnev [12]. They analyzed a vast set of available transport data for disordered organic materials and came to the conclusion that in some mysterious way energetic disorder is not important for the mobility temperature dependence. The strongest argument in support of this point of view is the independence of disorder magnitude $\sigma$ on the concentration of highly polar transport dopants. This is very unexpected because the dipolar contribution to the disorder should depend on the concentration of polar dopants. Schein and Tyutnev suggested that some intramolecular mechanism is responsible for the mobility temperature dependence.

We have analyzed essentially the same set of data but in a different manner and came to a very different conclusion. Our analysis shows that the dipolar contribution could be directly calculated from the temperature dependence of the slope $S$ of the mobility field dependence. Results of such calculations immediately demonstrate a reasonable agreement between experiment and theory, though available experimental data is extremely limited.

We have shown that a very popular method of the mobility calculation by the time of intersection of asymptotes to the plateau region and trailing edge of the transient is a possible reason why the calculations of $\sigma$ give misleading results. A simple yet accurate procedure of the mobility calculation and subsequent analysis of the mobility field and temperature dependences for evaluation of the disorder parameters has been discussed.

We would like to emphasize that a very significant contribution to the realization of the suggested program could be fulfilled by a simple recalculation of the mobility from already obtained transients (if available) and subsequent analysis of the mobility field dependence according to the lines suggested in the previous section. Also we would like to note that a direct access to the raw TOF data (current transients) should significantly improve our
ability to check consistency between experimental data and various theoretical models and would be considered as God’s gift by all theoreticians. Data for TOF transients could be provided as supplements to the experimental papers, this possibility is already provided by many leading scientific journals.

6 Acknowledgements

This work was supported by the ISTC grant 3718 and RFBR grants 05-03-90579-NNS-a and 08-03-00125-a. We are grateful to L. Schein and A. Tyutnev for giving us the opportunity to read their paper before publication.

Appendix. Mixed disorder in 1D model

Suppose that the total random energy $U(\vec{r})$ is a sum of two independent terms

$$U(\vec{r}) = U_{\text{dip}}(\vec{r}) + U_n(\vec{r}), \quad (14)$$

where $U_{\text{dip}}(\vec{r})$ is a dipolar contribution with the correlation function $C_{\text{dip}}(\vec{r}) = A_{\text{dip}}\sigma_{\text{dip}}^2 e^{\vec{a}\cdot\vec{r}}$, while the second term provides an additional energetic disorder with the correlation function $C_n(\vec{r}) = A_n\sigma_n^2 e^{\vec{a}_n\cdot\vec{r}}$, and $n > 1$. For independent disorder contributions the resulting correlation function is the sum of two terms

$$C(\vec{r}) = C_{\text{dip}}(\vec{r}) + C_n(\vec{r}). \quad (15)$$

In the 1D model the mobility is

$$\mu = \frac{D_0}{E \int_0^\infty dx \exp \left\{ -e\beta E x + \beta^2 [C(0) - C(x)] \right\}}, \quad (16)$$

where $D_0$ is a bare (microscopic) diffusion coefficient [6, 45]. For the case of strong disorder $\beta\sigma \gg 1$ a suitable tool for the calculation of integral 16 is a saddle point approximation. For example, eq 6 is a result of this approximation. In fact, for a pure dipolar disorder the PF dependence arises exactly in the case when this approximation is valid. In the saddle point approximation

$$\mu \propto \exp \left[ -C(0)\beta^2 + R(x) \right], \quad R(x) = ex\beta E + C(x)\beta^2, \quad C(0) = \sigma_{\text{dip}}^2 + \sigma_n^2, \quad (17)$$

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and \( x_s \) is a solution of the equation

\[
\frac{dR(x)}{dx} = e\beta E - A_{\text{dip}}\beta^2 \sigma_{\text{dip}}^2 \frac{a}{x^2} - nA_n \beta^2 \sigma_n^2 \frac{a^n}{x^{n+1}} = 0. \tag{18}
\]

Let us find when the mobility field dependence retains the PF form. This is the case when the third term in eq 18 is a small correction. If we retain the first two terms in eq 18 then the solution is

\[
x_s^0 = aZ = a \left( \frac{A_{\text{dip}}\beta^2 \sigma_{\text{dip}}^2}{e\beta aE} \right)^{1/2}, \tag{19}
\]

and the third term is a correction if

\[
A_{\text{dip}}\beta^2 \sigma_{\text{dip}}^2 \frac{a}{(x_s^0)^2} \gg nA_n \beta^2 \sigma_n^2 \frac{a^n}{(x_s^0)^{n+1}}, \quad \frac{nA_n}{A_{\text{dip}}} \frac{\sigma_n^2}{\sigma_{\text{dip}}^2} \frac{1}{Z^{n-1}} \ll 1. \tag{20}
\]

Saddle point approximation is valid if three conditions are valid

\[
-(\delta x_s)^3 \frac{d^3 R}{dx^3} \bigg|_{x=x_s^0} \ll 1, \quad \delta x_s \ll x_s^0, \quad x_s^0 \gg a, \tag{21}
\]

where \( \delta x_s = \left( \frac{d^3 R}{dx^3} \bigg|_{x=x_s^0} \right)^{-1/2} \). The first condition means that the Gaussian approximation is valid in the vicinity of the minimum of \( R(x) \), the second one means that the vicinity of the minimum does not reach the boundary of the integration domain, and the third one means that we can safely use power-law asymptotic for the correlation functions \( C(x) \). All inequalities could be condensed as

\[
1 \ll Z \ll \beta^2 \sigma_{\text{dip}}^2, \tag{22}
\]

and here and in future we drop all coefficients such as \( 3/\sqrt{2}, A_{\text{dip}}, \) or \( A_n \). This double inequality is equivalent to \( (\beta^2 \sigma_{\text{dip}}^2)^{-1} \ll ea\beta E \ll \beta^2 \sigma_{\text{dip}}^2 \). The low field boundary of the PF region can be estimated as \( Z_l \lesssim \beta^2 \sigma_{\text{dip}}^2 \). Substituting \( Z \) with \( Z_l \) in eq 20 we obtain eq 9 as a final necessary condition for the small contribution of the additional non-dipolar disorder in the low PF region \( ea\beta E \gtrsim (\sigma_{\text{dip}}^2 \beta^2)^{-1} \). The same estimation could be obtained by comparison of the dominant contribution to the mobility field dependence with the additional term \( \propto A_n \sigma_n^2 \).

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