Charge Carrier Transport in Disordered Polymers

S. V. Novikov
A.N. Frumkin Institute of Electrochemistry, Leninsky prosp. 31, Moscow 119071, Russia

Abstract

General properties of charge carrier transport in disordered organic materials are discussed. Spatial correlation between energies of transport sites determines the form of the drift mobility field dependence. Particular kind of spatial correlation in a disordered material depends on its nature. Mobility field dependences have to be different in polar and nonpolar materials. Different methods of mobility calculation from the shape of photocurrent transient are analyzed. A widely used method is very sensitive to the variation of the shape of the transient and sometimes produces results that effectively masquerade the true dependence of the mobility on electric field or trap concentration. Arguments in favor of the better, more reliable method are suggested. Charge transport in materials containing charged traps is considered without using the isolated trap approximation and this leads to qualitatively different results. They indicate that the effect of charged traps can hardly be responsible for experimentally observed transport properties of disordered organic materials.

Keywords: charge transport; correlated disorder; computer simulations

INTRODUCTION

Any feasible electronic application of a polymer material implies that the material can conduct an electric current via some kind of charge transport mechanism. Velocity of charge carriers (electrons or holes) may be an important parameter per se effectively determining operating characteristics of the device or it could influence other important parameters such as carrier injection or recombination efficiency. Some degree of structural disorder is present in most polymers currently used in real life applications, so they naturally belong to the general category of disordered organic materials. At the same time disordered low molecular weight organic materials often demonstrate similar general features of charge transport; for this reason in this article various properties of charge transport in disordered organic materials are mostly discussed without specific emphasis on polymeric nature of a material.

For many years the study of charge carrier transport in disordered organic materials was mostly motivated by hope to use them in various electronic and optoelectronic devices. At the same time this problem is an interesting and sometimes even intriguing area of modern condensed matter physics. Good review of the area may be found in recent monographs.¹²

We consider here only materials which are insulators under usual conditions and attain short-lived conductivity after injection of charge carriers under the action of laser pulse or electric discharge and completely leave aside such highly conducting materials as doped polyacetylene, polyaniline etc. Typical materials include low molecular weight organic glasses, polymers doped with aromatic organic molecules (usually amines or hydrazones), polysilanes, polyconjugated polymers, and other compounds. This diverse variety demonstrates a lot of common transport features unambiguously indicating a common transport mechanism.

Transport properties of materials are usually characterized by carrier drift mobility \( \mu \) and its dependence on applied electric field \( E \), temperature \( T \), and other relevant parameters.
The most direct method of the mobility measurement is the time-of-flight method (TOF) where carriers are generated at the vicinity of one electrode of the plane capacitor (organic material fills the space between electrodes) and then drift to the opposite electrode under the action of applied uniform electric field $E$. Analyzing the shape of the photocurrent transient, one can calculate the transit time $t_{tr}$ (the moment when current begins to drop, thus indicating arrival of carriers to the opposite electrode) and then the mobility

$$\mu = \frac{v}{E} \approx \frac{L^2}{V_0 t_{tr}},$$

where $L$ is thickness of the transport layer, $v$ is the average velocity of charge carriers, and $V_0$ is the applied voltage. Dominant majority of experimental data cited in this article was obtained by the TOF method.

Let us briefly summarize major experimental findings offering important clues on the nature of charge transport in such materials.\[1, 2, 3, 4\]

1) Molecularly-doped polymers offer a natural possibility to study dependence of the mobility on dopant concentration. It was found that

$$\ln \mu \approx -\frac{2R}{R_0},$$

where $R$ is the average distance between dopant molecules. This relation suggests that the transport occurs as a series of hops between localized states (transport sites) originating, in this particular case, at the dopant molecules. However, in some exceptional cases the radius $R_0$ of the wave function of a transport site is unreasonably large.\[5\]

2) Mobility increases exponentially with the increase of temperature. There is no consensus on the form of this dependence: some authors favor a simple activation dependence

$$\ln \mu \propto -\frac{1}{T},$$

while others argue that the dependence

$$\ln \mu \propto -\frac{1}{T^2}$$

is more accurate. It is generally accepted that an exponentially strong temperature dependence may be most naturally explained by suggesting that the major factor governing charge transport in disordered organic materials is an energetic disorder: random locations and orientations of molecules in the bulk of the material produce random fluctuations of site energies $U_i$. Then the dependence $\mu(T)$ should be connected with the density of states $P(U)$. There is no reason for $P(U)$ to maintain the same form in different materials and this may be the reason for different forms of $\mu(T)$.

3) The most surprising fact is the mobility field dependence. Indeed, for carrier hopping between spatially localized sites we should expect

$$\ln \mu \propto eER/k_B T,$$
just estimating a typical drop in the difference of carrier energy between two transport sites separated by the typical intersite distance \( R \). Yet instead of eq \( 5 \) an almost ubiquitous Poole-Frenkel (PF) dependence emerges in the materials

\[
\ln \mu \propto \sqrt{E},
\]  

leading to much stronger field dependence of the mobility in weak field. Uncertainty in the form of dependence \( \mu(T) \) is mostly originated from the difficulty to measure the quasi-equilibrium (nondispersive) mobility in a wide temperature range. In striking contrast to this limitation, dependence (6) was measured for some materials in really wide field range (an unrivaled example is ref. 6 with \( E \) varying from \( 8 \times 10^3 \) to \( 2 \times 10^6 \) V/cm).

For a long time an explanation of the PF dependence has been considered as a major problem for the charge transport theory. Since the early paper of Gill, who suggested an empirical formula

\[
\mu = \mu_0 \exp \left[ \gamma \left( \frac{1}{T} - \frac{1}{T_0} \right) \left( \sqrt{E} - \sqrt{E_0} \right) \right],
\]  

based on the study of charge carrier transport in polyvinylcarbazole, it was very tempting to attribute the field dependence of \( \mu \) to the influence of charged traps. In the case of trap-controlled charge transport with charged particles (having charge of the opposite sign to carriers) serving as traps, an applied electric field \( E \) leads to the decrease of activation energy of the carrier escape from a trap. In this case

\[
\gamma = \frac{2}{k_B} \left( \frac{e^3}{\varepsilon} \right)^{1/2}
\]  

(here \( \varepsilon \) is a dielectric constant) and calculated values of \( \gamma \) are usually close to the measured ones by the order of magnitude, though discrepancies by a factor of 2–3 are typical. Yet this classical PF mechanism attained a lot of criticism because there is no evidence for charged traps to be a common constituent in very different classes of disordered organic materials.

A first really successful transport model was the Gaussian Disorder Model (GDM). In the GDM transport sites are arranged on a regular lattice and are assigned site energies \( U_i \) drawn independently from a Gaussian distribution having variance \( \sigma^2 \). This model explained many features of charge transport in disordered organic materials, among them the temperature dependence of mobility, transition from the quasi-equilibrium transport to the dispersive-like with temperature decrease, and others features. Still the explanation of the PF field dependence remained an unsolved problem because the GDM can reproduce this dependence in the limited field range only, not significantly wider than \( 3 \times 10^5 \) – \( 1 \times 10^6 \) V/cm, in weaker field dependence \( \mu(E) \) has the usual form (5). Moreover, the only reason for the approximate PF dependence in the GDM is the Miller-Abrahams hopping rate. There is no reliable evidence that this particular rate is the universal hopping rate in a wide variety of disordered materials. For this reason it was highly desirable to retain all useful features of the GDM and yet incorporate some new feature permitting to explain the PF field dependence.
CHARGE TRANSPORT IN POLAR MATERIALS

A history of the GDM modification that eventually lead to the successful explanation of the PF dependence began with the study of dipolar contribution to the total energetic disorder in organic materials. Computer simulation of the distribution of energies for a carrier moving through a simple cubic lattice with sites occupied by randomly oriented dipoles (thus, the energetic disorder in this case originates from the electrostatic charge-dipole interaction) was carried out by Dieckmann, Bässler, and Borsenberger; they found that $P(U)$ has the Gaussian form for high concentration of dipoles and goes to the Lorentzian one for low dipole concentration. They calculated the energy variance $\sigma_d^2 = \langle U^2 \rangle$ and found that typical values of $\sigma_d$ are 0.05–0.1 eV which means that the dipolar contribution should be a significant part of the total $\sigma$ (according to the GDM, $\sigma \approx 0.1$ eV is needed to fit experimental temperature dependence of $\mu$). Later it was found that for this model of dipolar glass (DG) function $P(U)$ could be calculated analytically. For a simple cubic lattice

$$\sigma_d = 2.35 \frac{epc^{1/2}}{\varepsilon a^2}$$  \hspace{1cm} (9)

(here $a$ is a lattice scale, $p$ is a dipole moment, and $c$ is a fraction of sites occupied by dipoles) and the distribution of $U$, while indeed having the Gaussian form for $c \approx 1$, has the long tail $P(U) \propto 1/U^{5/2}$ for $c \ll 1$.

**Figure 1.** Distribution of site energies $U_i$ in a $50 \times 50 \times 50$ sample of the simple cubic lattice model of dipolar glass. Black and white spheres represent sites with positive and negative values of $U_i$, correspondingly, while the radius of a sphere is proportional to the absolute value of $U_i$. Sites with small absolute values of $U_i$ (less than $3ep/\varepsilon a^2$) are not shown for the sake of clarity.

The most significant property of the DG model is a strong spatial correlation in the
distribution of $U(\vec{r})$ and the energy correlation function decays very slowly with distance\textsuperscript{11}

$$C(\vec{r}) = \langle U(\vec{r})U(0) \rangle \approx 0.74 \sigma_d^2 a/r, \quad r \gg a \quad (10)$$

(here angular brackets denote statistical average). In a correlated Gaussian medium the conditional probability $P(U|U_0)$ which is the probability density to have energy $U$ at the site $\vec{r}$ if the site energy at the reference site $\vec{r}_0$ is $U_0$ has the form\textsuperscript{11}

$$P(U|U_0) = \frac{1}{\sqrt{2\pi\sigma^2_\delta}} \exp \left[ -\frac{1}{2\sigma^2_\delta} \left( U - C(\vec{r} - \vec{r}_0)/U_0 \right)^2 \right], \quad \sigma^2_\delta = \sigma^2_d - \frac{C^2(\vec{r} - \vec{r}_0)}{\sigma^2_d}. \quad (11)$$

Keeping in mind that $C(0) = \sigma^2_d$, we see that equation\textsuperscript{11} expresses the tendency of sites that are spatially close to have close energies, in striking contrast to the GDM case (see Fig.\textsuperscript{11}).

![Figure 2](image-url)

**Figure 2.** Computer simulation of the cluster distribution on size (squares - the GDM, triangles - DG model with same $\sigma$). Here $N$ is the number of sites in a cluster, $N_c$ is the number of clusters and $N_{tot}$ is the total number of sites; cluster is defined as a connected set of sites having energies greater than some (arbitrary) threshold energy ($3.7\sigma$ in this particular case).

Another manifestation of the correlated nature of DG is an exact result for the dependence of the distribution of average domain energy $U_V = \langle U \rangle_V$ on domain size $V$. For a Gaussian random medium without any spatial correlation the distribution has the Gaussian form with variance

$$\sigma^2_V = \sigma^2 a^3/V, \quad (12)$$

while for spherical domains in DG\textsuperscript{12}

$$\sigma^2_V = 12\sigma^2 a/5R, \quad (13)$$
where \( R \) is the radius of the domain. The difference between (12) and (13) suggests that large domains are much more common in dipolar matrix and, indeed, relative number of large clusters in DG is greater by many orders of magnitude in comparison with the uncorrelated medium (see Fig. 2).

At the same time Gartstein and Conwell suggested that a correlated nature of the energy landscape should significantly affect charge transport in disordered medium, effectively increasing the typical scale of the hop and, thus, enhancing mobility field dependence. The next major step was achieved by Dunlap, Parris, and Kenkre, who found that for charge carrier hopping in 1D random Gaussian energy landscape

\[
\mu = \frac{\mu_0}{e\beta E \int_0^\infty dy \exp \left( -e\beta E y + \beta^2 \left[ C(0) - C(y) \right] \right)}, \quad \beta = 1/k_B T. \tag{14}
\]

For the case of strong dipolar disorder \( \sigma_d \beta \gg 1 \) equation (14) gives

\[
\mu \approx \mu_0 \exp \left[ -\left( \sigma_d \beta \right)^2 + 2\left( \sigma_d \beta \right) \sqrt{e\alpha E} \right], \tag{15}
\]

and, in general, if \( C(\vec{r}) \propto 1/r^p \) then \( \ln \mu \propto E^{p/p+1} \). At last, computer simulation confirmed that the dipolar correlation leads to the PF mobility field dependence for 3D carrier transport (see Fig. 3) and on the basis of extended simulation an empirical relation was suggested

\[
\mu \approx \mu_0 \exp \left[ -\frac{9}{25} \left( \sigma_d \beta \right)^2 + 0.78 \left( \left( \sigma_d \beta \right)^{3/2} - 2 \right) \sqrt{e\alpha E/\sigma_d} \right]. \tag{16}
\]

Equations (15) and (16) have essentially the same dependence on \( E \) and \( T \) and only numerical coefficients are different. Thus, the simplified 1D model could serve for a quick estimation of the mobility field dependence in disordered materials.

Good qualitative description of charge transport in a correlated medium is presented in ref. 18. The principal difference between a correlated random medium and an uncorrelated one is that in correlated medium deepest valleys of the energetic landscape (having maximal escape time for a carrier at \( E = 0 \)) are also the widest. For this reason carrier escape time for such valleys decreases drastically for \( E > 0 \). For every magnitude of \( E \) a critical size \( R_c(E) \) exists such that valleys of this size are the most efficient for carrier capture. Simple calculation gives \( R_c \propto E^{-1/2} \) and \( R \) in eq (5) should be substituted for \( R_c(E) \). This is the physical reason for the PF dependence.

An attracting feature of the DG model is absence of any significant free parameter: the energy scale (i.e. \( \sigma \)) may be calculated using (9) provided \( p, a, \) and \( c \) are known. Still, numerical coefficients in eq (16) are certainly not constants (for example, they weakly depend on \( R_0 \)), so equation (16) should be considered rather as a guide and not as a strict relation for \( \mu(E, T) \) in any particular polar material.

Another important feature of the DG model is that, unlike the GDM, the form of the mobility field dependence for moderate field does not depend on the particular kind of hopping rate: for \( e\alpha \beta E/\sigma_d \lesssim 1 \) mobility dependence retains its PF form (even the slope is the same) for any nonpathological hopping rate.

It is worth to mention, though, that in (partially) orientationally ordered dipolar matrices correlation properties of the distribution of \( U_i \) may be very different. In such matrices transport properties may have nothing in common with the usual PF picture.
Figure 3. Mobility field dependence in the DG model for different values of $\sigma_d \beta$ (from top curve downward). The lowest curve is the mobility for the GDM for $\sigma \beta = 5.10$. If $\sigma_d = 0.1$ eV and $a = 10 \, \text{Å}$, then $eaE/\sigma_d \approx 1$ for $E = 10^6 \, \text{V/cm}$.

**CHARGE TRANSPORT IN NONPOLAR MATERIALS**

A vast collection of experimental data indicates that the model of dipolar glass cannot serve as a universal explanation for the PF mobility field dependence in disordered organic materials. If the reason for this dependence is the spatial correlation of the dipolar type $^{10}$, then it is absolutely impossible to explain the existence of the PF dependence in nonpolar materials, where it was routinely observed. $^{21, 22, 3, 23, 24}$ More close study of experimental data reveals, however, that in such materials the experimentally tested field range is not too broad (not significantly greater than one order of magnitude or even less) and, moreover, sometimes clearly visible deviations from straight lines can be observed when $\ln \mu$ is plotted against $E^{1/2}$. $^{23}$ In some cases these deviations lead to the upward convexity of the mobility curve, while in others they lead to the downward convexity. Quite formally, this behavior may be described by

$$\ln \mu \propto E^n$$

with $n$ being in some cases smaller than 0.5 and in some cases greater than 0.5. This observation hints that, quite possibly, in weakly polar organic materials the real mobility field dependence is not a true PF dependence, but rather a quasi-PF dependence with $n \neq 0.5$. This quasi-PF dependence can successfully imitate true PF dependence in not so wide field range. According to the result of 1D model, $^{23}$ the necessary condition for validity of relation (17) is the algebraic behavior of correlation function $C(r) \propto r^{-p}$. 

7
Quadrupolar Glass Model

One possible reason for such behavior is the contribution from randomly oriented quadrupoles. Quite frequently, transport molecules contain highly polar groups having significant dipole moments. These groups may be arranged in such a way that the total dipole moment of the molecule is close to zero, but the quadrupole moment of the molecule is large enough. For example, for the particular case of two identical groups having dipole moment \( p \), oriented in opposite directions and separated by distance \( d \), the total dipole moment of the molecule is exactly zero, but the quadrupole moment \( Q = pd \) is nonzero. In close analogy with the DG model\(^{11}\) we may consider the model of quadrupolar glass (QG), its simplest incarnation being a simple cubic lattice with sites occupied by randomly oriented quadrupoles\(^{25}\).

Calculation of the correlation function \( C(\vec{r}) \) for the QG model gives\(^{25}\)

\[
C(\vec{r}) \approx 0.5\sigma^2_q \left( \frac{a}{r} \right)^3, \quad r \gg a, \quad \sigma^2_q = C(0) = \frac{4e^2Q^2c}{5\varepsilon^2} \sum_m \frac{1}{r_m^6}.
\]

where \( c \) is the fraction of lattice sites, occupied by quadrupoles. If \( p = 3D, \varepsilon = 3, a = 10 \) Å, \( b = 5 \) Å, then for the totally filled lattice \( \sigma_q \approx 0.08 \) eV. In 1D approximation the carrier mobility in the QG model for the case of strong disorder \( (\sigma_q\beta)^2 \gg 1 \) has the form

\[
\mu \propto \exp \left[ -(\sigma_q\beta)^2 + \frac{2^{3/2}}{3^{1/4}} (ca\beta E)^{3/4} (\sigma_q\beta)^{1/2} \right]
\]

This particular field dependence can successfully imitate the PF dependence in not too wide field range \( E_{\text{max}}/E_{\text{min}} \lesssim 10 \). Moreover, there is another factor that can bring the quadrupole field dependence even closer to the PF dependence. This factor is an effect of dispersive transport: in dispersive regime \( \mu \propto E^\alpha \)\(^{26}\). If plotted as \( \ln \mu \) vs \( E^{3/4} \), the dispersive component bends the straight line, making the mobility curve convex upward, thus pushing field dependence more close to the PF one (contribution of the dispersive component is evident, for example, for photocurrent transient in the data of ref. \(^{22}\) even at high temperature).

Detailed computer simulation of the 3D charge transport in the QG model has not been carried out yet, but preliminary data unambiguously support the principal result of 1D model for the mobility field dependence \( \ln \mu \propto E^{3/4} \)\(^{24}\). Analogy with the DG model suggests that the functional type of the mobility dependence on \( E \) and \( T \) could be well captured by the 1D model, while numerical coefficients should be different. Extensive comparison of the QG model with experimental data is still absent, though preliminary analysis of transport data for nonpolar polysilanes indicates that dependence \( \ln \mu = a + bE^{3/4} \) is certainly not worse (in terms of statistical correlation coefficient \( R^2 \)) than the PF dependence\(^{28}\).

Los Alamos Model

Recently a new model was suggested to explain the PF mobility field dependence in nonpolar polyconjugated polymers such as polyphenylene vinylens (PPVs)\(^{29,30}\). According to this model, the major source of the energetic disorder in PPVs is almost static intramolecular
fluctuations of the torsion angle of benzene ring, resulting in the carrier energy fluctuations with the correlation function

\[ C(\vec{r}) \propto \frac{k_B T}{r} \exp(-\alpha r), \quad \alpha = s/K, \]  

(20)

where \( s \) is the intramolecular restoring force constant and \( K \) is the intermolecular restoring force constant. This function in the limit case \( \alpha \to 0 \) gives an appropriate behavior needed to provide the PF dependence. In densely packed PPVs typical values of \( \alpha \) should be small, and according to the 1D model the mobility field dependence has the form

\[ \ln \mu \propto -\sigma_t^2 \beta + \beta \sqrt{2\pi \sigma_t^2 e a E}, \quad \sigma_t^2 = \frac{\nu^2}{2\pi K a}, \]  

(21)

where \( a \) is the short-range cutoff and \( \nu \) is the linear electron-vibration coupling.

Field and temperature dependence of the mobility in the LA model is different (though not very different) from the prediction of the QG model. Thus, a careful study of the dependence of \( \mu \) on \( E \) and \( T \) may provide an opportunity to discriminate between these models. At present, there is no possibility to state which particular model better describes the mobility field dependence in nonpolar materials. We should note, though, that the model of quadrupolar glass does not rely on any particular property of the nonpolar material (apart from its quadrupolar nature). From this point of view it is preferable over LA model that, obviously, could hardly be applied for the explanation of the properties of various low molecular weight nonpolar organic glasses. These materials demonstrate the same PF field dependence as PPVs and can be perfectly well described by the QG model. High intramolecular flexibility is a necessary prerequisite for significant amplitude of the energetic disorder in the LA model, yet experimental data unambiguously demonstrate that some nonpolar materials consisting of very rigid molecules may still have significant energetic disorder (a good example of the material with planar rigid nonpolar molecules having \( \sigma \approx 0.09 \) eV is discussed in ref. [22]).

It is worth to add that the very observation that served as a first clue for the LA model, the significant difference between slopes of the PF dependence for two particular polyconjugated polymers - one is traditional MEH-PPV[31] and the other one (having very small slope of the mobility curve) is stiff-chain polyfluorene[32] - may be reasonably well explained using the QG model. Indeed, the local stiffness of the main polymer chain should by itself decrease the quadrupolar disorder. In addition, the molecule of polyfluorene contains only carbon and hydrogen atoms, while the molecule of more flexible MEH-PPV contains oxygen atoms as well - this means that the quadrupolar moment of the monomer unit for MEH-PPV is greater. Hence, both factors act in the same direction, decreasing the quadrupolar disorder in polyfluorene and weakening the mobility field dependence.

Recent papers on charge transport in PPVs offer a limited opportunity to compare QG and Los Alamos models[33,34]. These papers offer data on the temperature dependence of the PF coefficient \( b_{PF} = \gamma/T \) (see eq 8). By definition

\[ b_{PF} = \frac{\partial \ln \mu}{\partial E^{1/2}} \]  

(22)

and for the LA model \( b_{PF} \propto \beta \). Although in the QG model coefficient \( b_{PF} \) is not a true constant with respect to \( E \), its field dependence is very weak

\[ b_{PF}^{QG} \propto E^{1/4} \beta^{5/4} \]  

(23)
and we can approximately treat it as an effective constant. Results of the fit $b_{PF} \propto \beta^n$ are shown in Fig. 4.

![Figure 4](image_url)

**Figure 4.** The correlation coefficient $R^2$ obtained by fitting the temperature dependence of $b_{PF}$ for different PPVs on $n$ in $b_{PF} \propto \beta^n$. The best fit corresponds to the minimum of $1 - R^2$. Curves for different PPVs from ref. [34] are marked A, B, C, and D; curve A’ represents data from ref. [33] (the same PPV as for the curve A, but different thickness of the transport layer).

For most PPVs the best $n$ is close to 1.5 and, thus, more close to 1.25 (QG model) than to 1 (LA model). A possible reason for the discrepancy with the QG model may be the specific technique used in refs. [33,34] where mobility was calculated from the current-voltage characteristics in the space-charge limited conduction regime assuming the PF mobility field dependence. Thus, the mobility field dependence was not calculated at all, only the coefficient $b_{PF}$ was optimized to fit experimental current-voltage curves. The direct study of the temperature dependence of the corresponding true QG coefficient

$$b_q = \frac{\partial \ln \mu}{\partial E^{3/4}}$$

obtained from TOF experiments should be a better way to test the QG model.

**Mixed Disorder: Is It Possible to Provide a Simple Formula for the Mobility Field Dependence?**

In a typical case the total energetic disorder in a material has several contributions of different nature

$$U_{tot}(\vec{r}) = \sum_s U_s(\vec{r})$$

(say, dipolar and quadrupolar components). In such situation the correlation function (assuming statistical independence of individual components) is a sum of terms having different
dependence on distance. The resulting mobility dependence in the 1D model has the form

$$1/\mu \propto \int_0^\infty dy \exp \left( -eE\beta y + \beta^2 \sum_s [C_s(0) - C_s(y)] \right),$$  \hspace{1cm} (26)

which cannot be written in the form of an explicit simple formula for nontrivial functions \(C_s(y)\).

Moreover, mobility field dependence could present a clear indication of the existence of several contributions to (25) only when mobility is measured in an exceptionally wide field range. Careful analysis shows that calculation of individual dipolar and quadrupolar contributions to the total disorder could be performed only in the case when mobility field dependence is measured in the field range spanning at least three orders of magnitude.\cite{35}

This is hardly possible in real experiments.

**TRAP-CONTROLLED CHARGE TRANSPORT**

Most organic materials contain impurities serving as traps for charge carriers (i.e. such impurities have energy levels laying deeper than levels of majority of transport sites). Typically, energies of trap sites have no spatial correlation and produce an additional spatially uncorrelated disorder. Important question is: to what extent general properties of charge transport in correlated medium are insensitive to the presence of traps (later we will limit our consideration to the particular case of dipolar medium)? This problem has been extensively studied in the 1D approximation and by means of 3D computer simulation.\cite{25}

Again, major results are the same for both approaches and may be summarized as follows:

1) addition of traps leads to the decrease of the carrier drift mobility;

2) PF dependence in weak fields remains unchanged without respect to trap depth \(\Delta\) and concentration \(c\);

3) in stronger fields a linear field dependence \(\ln \mu \propto E\) emerges.

These conclusions seem to be in striking contradiction with recent experimental observations for transport of holes in doubly doped polymer layers.\cite{36,37,38} Molecules of one dopant, added in small concentration, and possessing significantly lower ionization potential, served as traps for charge carriers. In these studies it was found that for shallow traps the PF dependence remains mainly untouched,\cite{36,37} while for deep traps a linear field dependence was observed in the whole field range.\cite{36} The most puzzling experimental result is the unusual dependence of the mobility on trap concentration \(\mu \propto 1/c^n\),\cite{36,38}

with \(n > 1\) instead of expected dependence with \(n = 1\) for trap-controlled transport. Again, this result does not agree with the theoretical dependence where \(n = 1\).\cite{25}

Quite unexpected solution for all these puzzles was suggested in ref.\cite{39} Surprisingly, the problem is not connected with any fault of the theory or inaccuracy of modern experimental technique but rather with the interpretation of the experimental data, namely with
Figure 5. Two methods of mobility calculation from experimentally measured photocurrent transient: 1) $\mu_i = L/t_i E$ where $t_i$ is the time of intersection of asymptotes to the plateau and trailing edge of the transient; and 2) $\mu_{1/2} = L/t_{1/2} E$ where $t_{1/2}$ is the time for photocurrent to decay to the half of its plateau value.

the particular way of the mobility calculation from the photocurrent transient temporal dependence.

In TOF experiment, mobility is usually calculated by two methods (Fig. 5). The first method is the method of choice for most experimental papers. Unfortunately, this particular method is too sensitive to the variation of the shape of the transient with variation of $E$ (or $c$) and tends to overestimate the contribution of fast under-relaxed carriers. The second method produces mobility that is much more close to the strict definition of the mobility as $\mu_v = \langle v \rangle / E$ where $\langle v \rangle$ is an average carrier velocity. The sensitivity of the first method is so significant that even in the case when good current plateau with $I(t) \approx \text{const}$ is observed in the whole range of variation of the parameter (e.g., $E$), there is a possibility to obtain principally different mobility field dependences for $\mu_i(E)$ and $\mu_{1/2}(E)$ (see Fig. 5). Note, that for this particular case in the whole field range the transient is more or less nondispersive and has a well-defined plateau (Fig. 7). We can conclude that in some cases mobility, calculated by the first method, effectively masquerades a real field dependence of the true mobility. The same reason explains an unusual dependence of the mobility on trap concentration.

The second method produces much more reliable results and should be used instead of the first one. This conclusion is in sharp contradiction with the common belief that field dependences of $\mu_i$ and $\mu_{1/2}$ are essentially the same (experimental evidence for the difference may be found in literature, but it is usually ignored). The use of $\mu_{1/2}$ is especially important in situations where we have to choose among not very distinctive alternatives, such as QG or PF mobility field dependence in nonpolar materials.
Figure 6. Mobility field dependence for dipolar glass with traps for $\sigma\beta = 3.83$, $\Delta\beta = 10$, $c = 0.01$, and $L = 40,000$ lattice planes (equivalent to transport layer thickness of 30-40 $\mu$m) for different methods of mobility calculation: $\mu_v$ - diamonds, $\mu_{1/2}$ - triangles, and $\mu_i$ - squares. Here $c$ is a fraction of sites occupied by traps.

POOLE-FRENKEL MECHANISM REVISED:
EFFECT OF CHARGED TRAPS

Original PF mechanism was for a long time considered unacceptable for explanation of the mobility field dependence in disordered organic materials due to absence of charged traps (arguments provided in ref. 6 suggested that trap density is certainly less than $10^{13}$ cm$^{-3}$). Yet in a recent paper the PF model was revitalized by Rackovsky and Scher, who argued that a very low density of Coulomb traps is enough to produce an essentially nondispersive PF charge transport (they estimated that $10^{11}$-$10^{13}$ cm$^{-3}$ should be a sufficient density for transport layer with the thickness of 10 $\mu$m). Because such low density can easily avoid detection, they suggested that the PF model still can be considered as a possible candidate for explanation of charge transport in disordered organic materials.

Calculation of the PF effect in ref. 40 was carried out for the usual case of an isolated Coulomb trap only. Yet charged traps produce strongly spatially correlated energy landscape, and the hopping charge motion in such landscape usually has many features that cannot be captured by the approximation taking into account interaction of charge carrier with the isolated force center.

Early indication that charge transport in charged medium may significantly differ from predictions of the model of isolated Coulomb trap was presented by Dunlap and Novikov. In recent papers this problem has been considered in more detail for a special case of the medium with equal concentration of randomly located positive and negative traps.
The result is in drastic contrast with the approximation of isolated Coulomb trap. For example, at $E = E_{\text{crit}} = 4\pi n_0 e^2/\varepsilon^2$ (here $n_0$ is trap density) a transition from mobile to immobile carriers occurs and average carrier velocity $\langle v \rangle = 0$ for $E < E_{\text{crit}}$ in the infinite medium, so in finite transport layers the only possible regime is a dispersive transport with mobility depending on thickness.

By accident, mobility field dependence for $E < E_{\text{crit}}$ retains the PF form, but its temperature dependence and, more important, concentration dependence differ drastically from the prediction of the isolated trap model. For small concentration of traps

$$\ln \mu \approx -P(c, \beta) + 2 [e\alpha (E - E_{\text{crit}}) Q]^{1/2},$$

$$P(c, \beta) = \frac{4\pi h_a^3}{3(\ln c)^2}, \quad Q(c, \beta) = -\frac{8\pi h_a^4}{3(\ln c)^3}, \quad h_a = \frac{e^2 \beta}{\varepsilon a}.$$  

Here the lattice version of the model is considered assuming that fraction of sites occupied by charges is small $c \ll 1$ but $c \exp h_a \gg 1$.

Experimental test of the mobility dependence on the concentration of charged traps should be the best test of the result \cite{28}. By now there are no experimental data on this dependence (actually, no experimental data at all on charge transport in disordered organic materials containing controllable concentration of static charges; quite possibly, such data are very difficult to obtain). Nonetheless, the mobility temperature dependence \cite{28} seems to be too strong to describe existing experimental data. For this reason we believe that the model of charged traps cannot be suggested as a serious candidate for explanation of charge transport in disordered organic materials.
CONCLUSIONS

All variety of disordered organic materials could be subdivided into different classes on the basis of their spatial correlation properties in the distribution of energies of transport sites. Materials from different classes have different transport properties though differences are not very pronounced. In order to discriminate between different classes of the mobility field and temperature dependence, analysis of experimental data should be carried out with utmost care. In this respect an early attempt to characterize all materials in a unified manner (the Gaussian Disorder Model) is unjustified while we can now understand, why it was so successful. To some extent charge transport theory is ahead of experiment: major predictions (mostly concerning charge transport in nonpolar materials) still lack experimental test. For example, the reasonable question is: which model, quadrupolar glass or Los Alamos, is more suitable to describe charge transport in nonpolar PPVs? A careful and purposeful experimental study of the transport properties of nonpolar materials could resolve this problem.

Acknowledgements I am greatly indebted to A.V. Vannikov, P.M. Borsenberger, D.H. Dunlap, P.E. Parris, V.M. Kenkre, H. Bässler, A. Kadaschuk, and Z. Soos for numerous discussions. I am especially indebted to S. Nespurek for providing me with data on transport properties of polysilanes. Partial financial support of the International Science and Technology Center grant 2207 and the Russian Fund for Basic Research grant 02-03-33052 is acknowledged. This work was partially supported by the University of New Mexico and utilized the UNM-Alliance LosLobos Supercluster at the Albuquerque High Performance Computing Center.
REFERENCES AND NOTES

1. Pope, M.; Swenberg, C. E. Electronic Processes in Organic Crystals and Polymers; Oxford University Press: New York, 1999.
2. Borsenberger P.M.; Weiss, D.S. Organic Photoreceptors for Imaging Systems; Marcel Dekker: New York, 1997.
3. Borsenberger, P.M.; Magin, E.H.; Van der Auweraer, M.; De Schryver, F.C. Phys Status Solidi A 1993, 140, 9-47.
4. Bässler, H. Phys Status Solidi B 1993, 175, 15-56.
5. Schein, L.B.; Borsenberger, P.M. Chem Phys 1993, 177, 773-781.
6. Schein, L.B.; Peled, A.; Glatz, D. J Appl Phys 1989, 66, 686-689.
7. Gill, W.G. J Appl Phys 1972, 43, 5033-5040.
8. Novikov, S.V.; Dunlap, D.H.; Kenkre, V.M.; Parris, P.E.; Vannikov, A.V. Phys Rev Lett 1998, 81, 4472-4475.
9. Dieckmann, A.; Bässler, H.; Borsenberger, P.M. J Chem Phys 1993, 99, 8136-8141.
10. Novikov, S.V.; Vannikov, A.V. JETP 1994, 79, 482-485.
11. Novikov, S.V.; Vannikov, A.V. J Phys Chem 1995, 99, 14573-14576.
12. Novikov, S.V. Phys Status Solidi B 2000, 218, 43-46.
13. Novikov, S.V.; Vannikov, A.V., Mol Crystals and Liquid Crystals 1998, 324, 177-182.
14. Gartstein, Yu.N.; Conwell, E.M. Chem Phys Lett 1995, 245, 351-358.
15. Dunlap, D.H.; Parris, P.E.; Kenkre, V.M. Phys Rev Lett 1996, 77, 542-545.
16. Novikov, S.V.; Vannikov, A.V. SPIE Proc 1996, 2850, 130-138.
17. Novikov, S.V.; Vannikov, A.V. Synth Met 1997, 85, 1167-1168.
18. Dunlap, D.H.; Kenkre, V.M.; Parris, P.E. J Imag Sci Technol 1999, 43, 437-443.
19. Parris, P.E. J Chem Phys 1998, 108, 218-226.
20. Novikov, S.V.; Vannikov, A.V. SPIE Proc 1997, 3144, 100-109.
21. Borsenberger, P.M.; Gruenbaum, W.T.; Magin, E.H. Physica B 1996, 228, 226-232.
22. Borsenberger, P.M.; Gruenbaum, W.T.; Magin, E.H. Phys Status Solidi B 1995, 190, 555-563.
23. Sinicropi, J.A.; Cowdery-Corvan, J.R.; Magin, E.H.; Borsenberger, P.M. Chem Phys 1997, 218, 331-339.
24. Heun, S.; Borsenberger, P.M. Chem Phys 1995, 200, 245-255.
25. Novikov, S.V.; Dunlap, D.H.; Kenkre, V.M., SPIE Proc 1998, 3471, 181-191.
26. Scher, H.; Montroll, E.W. Phys Rev B 1975, 12, 2455-2477.
27. Novikov, S.V.; Vannikov, A.V., Mol Crystals and Liquid Crystals 2001, 361, 89-94.
28. Nespurek, S. Private communication.
29. Yu, Z.G.; Smith, D.L.; Saxena, A.; Martin, R.L.; Bishop, A.R. Phys Rev Lett 2000, 84, 721-724.
30. Yu, Z.G.; Smith, D.L.; Saxena, A.; Martin, R.L.; Bishop, A.R. Phys Rev B 2001, 63, 085202.
31. Campbell, I.H.; Smith, D.L.; Neef, C.J.; Ferraris, J.P. Appl Phys Lett 1999, 74, 2809-2811.
32. Redecker, M.; Bradley, D.D.C.; Inbasekaran, M.; Woo, E.P. Appl Phys Lett 1998, 73, 1565-1567.
33. Blom, P.W.M.; de Jong M.J.M.; van Munster M.G. Phys Rev B 1997, 55, R656-R659.
34. Martens, H.C.F.; Blom, P.W.M.; H. F. M. Schoo, H.F.M. Phys Rev B 2000, 61, 7489-7493.
35. Novikov, S.V. Proceedings of NIP15: International Conference on Digital Printing Technologies; Society for Imaging Science and Technology: Orlando, FL, 1999; 683-686.
36. Veres, J.; Juhasz, C. Phil Mag B 1997, 75, 377-387.
37. Wolf, U.; Bässler, H.; Borsenberger, P.M.; Gruenbaum, W.T. Chem Phys 1997, 222, 259-267.
38. Lin, L.B.; Borsenberger, P.M.; Magin, E.H.; Visser, S.A.; Gruenbaum, W.T. SPIE Proc 1998, 3471, 174-180.
39. Novikov, S.V. J Imag Sci Technol 1999, 43, 444-449.
40. Rackovsky, S.; Scher, H. J Chem Phys 1999, 111, 3668-3674.
41. Dunlap, D.H.; Novikov, S.V. SPIE Proc 1997, 3144, 80-91.
42. Novikov, S.V. Proceedings of NIP17: International Conference on Digital Printing Technologies; Society for Imaging Science and Technology: Fort Loderdale, FL, 2001; 764-767.
43. Novikov, S.V. Phys Status Solidi B 2003, in press.
44. The case of charged medium with unequal concentrations of positive and negative traps is unusual because in this medium energetic disorder is spatially inhomogeneous and the nondispersive charge transport is not possible at all.