

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/257936921>

# Diffusivity and mobility of non-equilibrium carriers in organic semiconductors: Existence of critical field determining temperature dependence

**DATASET** *in* JOURNAL OF APPLIED PHYSICS · OCTOBER 2013

Impact Factor: 2.18 · DOI: 10.1063/1.4824747

---

READS

50

**3 AUTHORS**, INCLUDING:



**Durgesh Chand Tripathi**

Indian Institute of Technology Kanpur

**15** PUBLICATIONS **32** CITATIONS

SEE PROFILE



**Y. N. Mohapatra**

Indian Institute of Technology Kanpur

**111** PUBLICATIONS **643** CITATIONS

SEE PROFILE



**Diffusivity and mobility of non-equilibrium carriers in organic semiconductors:  
Existence of critical field determining temperature dependence**

Durgesh C. Tripathi, Dharendra K. Sinha, and Y. N. Mohapatra

Citation: [Journal of Applied Physics](#) **114**, 154508 (2013); doi: 10.1063/1.4824747

View online: <http://dx.doi.org/10.1063/1.4824747>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/114/15?ver=pdfcov>

Published by the [AIP Publishing](#)

---

**Advertisement:**



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



# Diffusivity and mobility of non-equilibrium carriers in organic semiconductors: Existence of critical field determining temperature dependence

Durgesh C. Tripathi,<sup>1,2</sup> Dharendra K. Sinha,<sup>1,2</sup> and Y. N. Mohapatra<sup>1,2,3,a)</sup>

<sup>1</sup>Department of Physics, Indian Institute of Technology Kanpur, Kanpur 208 016, India

<sup>2</sup>Samtel Centre for Display Technologies, Indian Institute of Technology Kanpur, Kanpur 208 016, India

<sup>3</sup>Materials Science Programme, Indian Institute of Technology Kanpur, Kanpur 208 016, India

(Received 23 July 2013; accepted 24 September 2013; published online 16 October 2013)

The role of disorder in controlling diffusivity and mobility of charge-carriers in the hopping regime of transport within a potential landscape has become especially significant for organic semiconductors. The temperature and field dependence of diffusivity ( $D$ ) and mobility ( $\mu$ ) of injected charge-carriers have been simultaneously measured using electroluminescence transients for representative organic thin-films of tris(8-hydroxyquinoline) aluminum (III) (Alq<sub>3</sub>) and poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO). Significantly, the field dependence of diffusivity at different temperatures is similar except for a shift of a critical field beyond which it shows a sharp increase. The critical field is shown to be linearly decreasing with temperature ultimately vanishing at a characteristic limit  $T^*$ , and the slope is a measure of the localization length. The normalization of diffusivity is used to demonstrate the role of field in controlling temperature dependence. The scheme has been used to neatly decouple contributions from energetic (diagonal) and positional (off-diagonal) disorder thus enabling independent experimental determination of all the parameters of standard and correlated versions of Gaussian disorder model. The results demonstrate the validity of Gaussian disorder model even for non-equilibrium carriers, and that the parameters can be obtained with appropriate scaling of the field in such cases. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824747>]

## I. INTRODUCTION

The emergence of molecular semiconductors in the form of conjugated polymers and small molecules has revolutionized large area electronics through applications, such as organic light-emitting displays (OLEDs), organic thin-film transistors (OTFTs), and organic solar cells.<sup>1</sup> In all these applications, the active layer in the devices involves transport of charge-carriers in disordered thin-films of typically 100 nm or less, and hence over the last three decades, there has been considerable focus on understanding the physics of transport parameters of which charge-carrier mobility ( $\mu$ ) has been the most studied.<sup>2</sup> The current paradigm of transport models in these classes of materials is the Gaussian disorder model (GDM) with its many variants and extensions,<sup>3–9</sup> so named because the density of states (DOS) is considered to be Gaussian due to random disorder as in

$$g(E) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left(-\frac{E^2}{2\sigma^2}\right), \quad (1)$$

where  $E$  is the energy,  $N$  the site concentration, and  $\sigma$  the variance. Most insights for transport under GDM have come from detailed Monte-Carlo simulations incorporating microscopic processes of hopping, i.e., jumps through thermally assisted tunneling (as in Miller-Abrahams rates).<sup>10</sup> It has

been shown that an understanding of the temperature ( $T$ ) and field ( $F$ ) dependence of mobility is facilitated by the identification of a transport level above which carriers contribute to current, and an equilibrium level at  $-\sigma^2/k_B T$  below which carriers are essentially trapped.<sup>3,4,11,12</sup> The gap between these two levels depends on the variance of the distribution  $\sigma$  and the temperature  $T$ . A common feature of field dependence of mobility in these materials is that it exponentially depends on  $F^{1/2}$ , which is often termed in the literature as Poole-Frenkel (P-F) type dependence.<sup>3–5</sup> The disorder in these materials can be viewed as a combination of energy barrier fluctuations at each site (diagonal disorder) and randomness in relative positions of the sites (positional or off-diagonal disorder).<sup>3,4</sup> The field dependence of mobility is sensitive to both types of disorder and the temperature. There are excellent reviews of different approaches to such studies in the literature.<sup>2–4,7,8</sup> On the basis of GDM for very dilute non-interacting case, Bäessler and co-workers have proposed the following widely used temperature and field dependence of mobility, which is parameterized by  $\sigma$  and  $\Sigma$  as the extent of diagonal and off-diagonal disorder, respectively, as<sup>3,4</sup>

$$\mu_{GDM}(F, T) = \mu_{o,\infty} \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right] \times \exp\left[C\left\{\left(\frac{\sigma}{k_B T}\right)^2 - (\Sigma)^2\right\}\sqrt{F}\right], \quad (2)$$

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: [ynm@iitk.ac.in](mailto:ynm@iitk.ac.in)

where  $k_B$  is the Boltzmann constant,  $C$  a numerical constant, and  $\mu_{o,\infty}$  the zero field mobility at infinite temperature. Since most experimental data display such dependence within the limited range of temperature and field typical of experiments, the physically significant parameters of Eq. (2) are obtained by multi-parameter fitting. For some cases, the basic GDM has been modified by including long-range correlations, such as charge-dipole interactions,<sup>5</sup> and is termed as Correlated Disorder Model (CDM), wherein the functional dependence of mobility on temperature and field remains the same with modified parameters. It is to be noted that the temperature dependence at a fixed field is not predicted to be of Arrhenius type in these Gaussian DOS based models though many experiments do report Arrhenius behavior, and some of them can be fitted to both types of behavior within limited range of datasets.<sup>7,8,11</sup> Such models have now been sought to be extended to incorporate concentration dependence, especially for high concentration of carriers involved in OTFT applications, in which case the models are referred to as extended GDM (EGDM) or extended CDM (ECDM).<sup>6-9</sup> There is considerable debate on how the temperature dependence of mobility changes according to these models.<sup>7,8,12</sup> Apart from multi-parameter fitting, truly *independent* measurement of the whole set of parameters for any such model from experiments has been difficult. These models are generally valid when the carrier distribution settles down to quasi-equilibrium. In many experiments and device applications, this is not true since depending on the time window, relaxation within the DOS is concurrent with transport.<sup>4,13</sup> It is also not known to what extent these descriptions that are valid for quasi-equilibrium conditions, need to be modified for *non-equilibrium* transport.

Furthermore, there has been a lack of experimental studies on the other most significant transport parameter, namely, diffusivity ( $D$ ) of the carriers which should be related to mobility through generalized Einstein relation  $D/\mu = \chi(k_B T/e)$ , where  $\chi$  is the thermodynamic coefficient<sup>14-19</sup> and is unity for traditional non-degenerate semiconductors in equilibrium.<sup>19-24</sup> But for organic semiconductors, it has been shown that  $\chi$  can deviate substantially from unity and its variation is attributed to the shape and nature of DOS, degree of removal from equilibrium, and the role of deep levels during transport.<sup>14-21,23,24</sup> By now, the importance of diffusion in all the relevant applications is very well appreciated in the literature, but no cogent way for accounting for its dependences is as yet clear even from simulations. As a result, the measurement and understanding of diffusivity have assumed critical significance though it has been difficult since it is not accessible directly in most experiments.

Experimentally, one of the most popular methods of measurement of mobility has been the time-of-flight (TOF) technique which involves monitoring the current transient during the transport of injected charge-carriers over thicknesses of several microns.<sup>4,20,21</sup> In such experiments, the existence of non-dispersive transport is typically inferred from the occurrence of a flat plateau due to drift. But anomalously large dispersion is observed from the tail part of transients attributed to dispersion and field-assisted diffusion. From the analysis of such experiments, there has been a long standing

expression of the insight that diffusion during transport is more sensitive to disorder than the drift mobility, or that the mobility settles down to its stable value much more quickly than does the diffusivity in presence of disorder.<sup>13,20,25</sup> Therefore, the mechanisms of field dependent diffusion continue to be studied as an enigma in these materials. In contrast to TOF experiments, if electro-luminescence transient (ELT) technique is used, the thicknesses are typically less than 100 nm. The transport in such a case may occur in a highly non-equilibrium situation, and hence may provide opportunity to study both diffusion and dispersion in more detail as has been attempted recently with focus on non-equilibrium transport.<sup>16,25</sup> There have been many theoretical studies on the possible field dependence of diffusivity, but a definitive comparison with experiment has not been possible.<sup>16,23,24</sup> The inter-link between dispersion in energy and diffusion in space during transport has been appreciated but its interpretation has been difficult.<sup>24</sup> For practical applications of devices, such as in an OLED, the case of non-equilibrium is indeed the most relevant regime.

We have recently used ELT technique to simultaneously measure mobility and diffusivity of injected carriers.<sup>16</sup> This has opened up possibilities of answering many vexing questions regarding transport in organic semiconductors which were earlier possible only through simulation studies. The technique is based on noting that when a sheet of charge-carriers is injected high into the transport states, the packet of charge-carriers diffuses while drifting. The delay time between the injection and the detection of electroluminescence for a particular field gives the duration of drift, from which mobility is calculated as per conventional ELT analysis.<sup>16,26</sup> Beyond a characteristic field, however, the luminescence transient is sharply peaked whose tail for longer times (see Fig. 1, and Fig. S2 in supplemental material) yields the diffusion constant in a straightforward analysis as already shown<sup>16</sup> and described in supplemental material.<sup>26</sup>

The study of transport in disordered organic semiconductors therefore poses major challenges (i) due to interrelated temperature and field dependence arising from coupling of diagonal and off-diagonal disorder, (ii) in dealing with non-equilibrium conditions, and (iii) critically due to the lack of reliable experimental measurements of

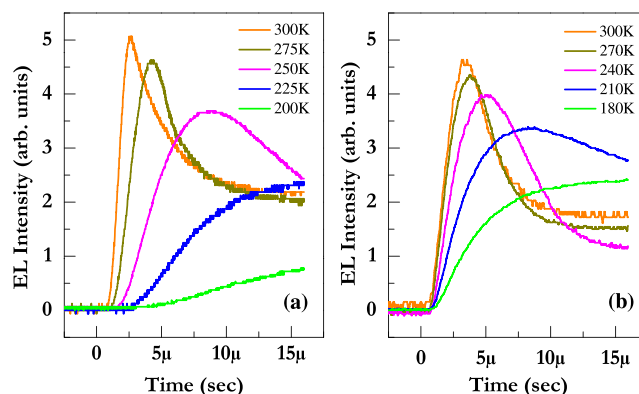


FIG. 1. ELT curves at a constant magnitude of voltage pulse for different temperatures (a) for Alq<sub>3</sub>/LiF/Al device at 13 V and (b) for PFO/Ca/Al device at 5 V.

diffusivity. Unlike mobility, to the best of our knowledge, there have been no studies on any organic semiconductor for which *both temperature and field dependence* of mobility and diffusivity have been measured *simultaneously*. In this paper, we do so for non-equilibrium carriers with devices typical of applications. We show that a completely different perspective emerges from the study of such dependences through direct measurements. To emphasize the generality of this view, we have deliberately chosen two well-characterized materials [tris(8-hydroxyquinoline) aluminum (III) (Alq<sub>3</sub>) and polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO)] so as to include one of each from the class of small molecules and polymeric semiconductors. We show that field dependence of diffusivity at any temperature beyond a critical field is similar, which when accounted for, leads to a unified description of mobility from which all the parameters of GDM (or CDM) transport models can be inferred independently. Moreover, the very existence of a critical field, which is heuristically equivalent to temperature, bears a clear empirical signature of the interplay between field and temperature for non-equilibrium carriers hopping in a Gaussian DOS. This also leads to the separation of the disorder parameters related to energy and position, i.e.,  $\sigma$  and  $\Sigma$ , respectively, where hot carriers serve as a probe for the potential landscape.

## II. EXPERIMENTAL DETAILS

In this work, we used two well characterized organic semiconductors viz. small molecule Alq<sub>3</sub> and polymer PFO which is end capped with dimethylphenyl. The high purity materials were obtained from commercial sources. The patterned indium tin oxide (ITO) substrates were RCA cleaned and treated under the oxygen-argon plasma prior to the active-layer deposition. The Alq<sub>3</sub> diode was fabricated in a state-of-the-art automated multi-chamber vacuum deposition. A hole injecting layer of 4,4',4''-tris[N-(3-methylphenyl)-N-phenylamino] triphenylamine (m-MTDATA) doped with tetrafluoro-tetracyano-quinodimethane (F<sub>4</sub>-TCNQ) is deposited followed by Alq<sub>3</sub> layer resulting a device structure ITO|m-MTDATA|Alq<sub>3</sub>|LiF|Al where LiF|Al serves as cathode. For polymer device, the PFO was dissolved in toluene and spin cast on ITO substrate, pre-coated with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). All solution processing was carried out in a nitrogen glove-box and dried in high vacuum at 120 °C for 2 h. The calcium (Ca) and aluminum (Al) cathodes were sequentially evaporated in high vacuum system. The device structure thus obtained was ITO|PEDOT:PSS|PFO|Ca|Al. The thickness of the active-layer was determined using a profilometer (Tencor alpha-Step 500) for data analysis.

The device was mounted on the cold finger of a cryostat maintained at  $10^{-3}$  mbar of pressure immediately after fabrication. For temperature dependent electrical measurements, Lakeshore 370 was used as temperature controller, and additional care was taken to mount a separate silicon diode close to the sample to ensure temperature calibration. For ELT measurements, voltage pulses of varying magnitude were applied across the device using a pulse generator (50 MHz HP 81101 A) with rise time 10 ns. The time

dependent electroluminescence signal was recorded using a photomultiplier tube (S100, response time < 1 ns) which was connected to a digital oscilloscope (500 MHz HP 54615B) with proper pulse matching for pulse shape fidelity. The details of the experiment and the analytical technique for determining mobility and diffusivity are discussed in the supplemental material.<sup>26</sup>

## III. RESULTS AND DISCUSSION

### A. ELT features: Temperature dependence

Figure 1 shows ELT curves for the two different materials under study for different temperatures keeping the bias across the device constant. For a fixed temperature, a similar set of curves is obtained for varying fields as has been shown previously.<sup>16</sup> The transport parameters in these cases refer to electrons (negative polarons) for Alq<sub>3</sub> and holes (positive polarons) for PFO assuming the validity of usual asymmetry of mobility for the two type of carriers in these materials. For a particular field chosen, when temperature is low such that one is unable to inject sufficient excess charges to the transport states, no peak results and one can get only mobility from the delay time. The anomalously broad threshold has long been a puzzling feature observed in disordered semiconductors and has been explained to be due to dispersion.<sup>25</sup> At higher temperatures, the threshold rise becomes sharp (negligible dispersion) reaching a peak and then decays slowly to a plateau. We have previously argued that in this regime, the peak and tail structure are due to diffusion of (hot) carriers from the high concentration front rapidly advancing towards the other electrode.<sup>16</sup> In other words, it can be thought of as a developing carrier diffusion profile in an inertial frame moving with a constant drift-velocity where the advancing front surface acts as the source of the carriers. In this case, diffusivity of the drifting hot carriers can be easily derived from the line shape as shown in the supplemental material.<sup>26</sup>

### B. Mobility and diffusivity: Field and temperature dependence

Figure 2 shows the results for Alq<sub>3</sub> at different temperatures where  $\log \mu$  and  $\log D$  are plotted against  $F^{1/2}$ , as is conventional for P-F type field dependence, and field is

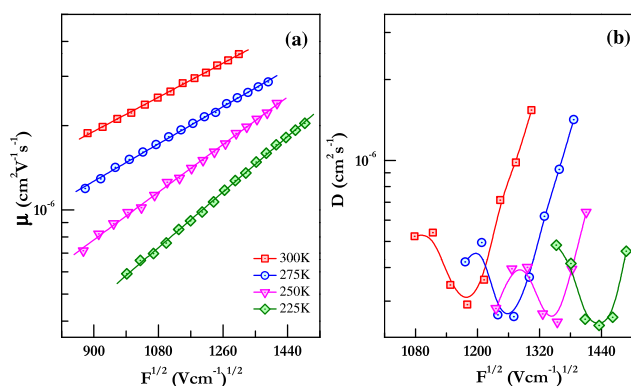


FIG. 2. Field dependence of (a) mobility and (b) diffusivity of ITO[p-MTDATA|Alq<sub>3</sub> (65 nm)|LiF|Al] device at different temperatures.



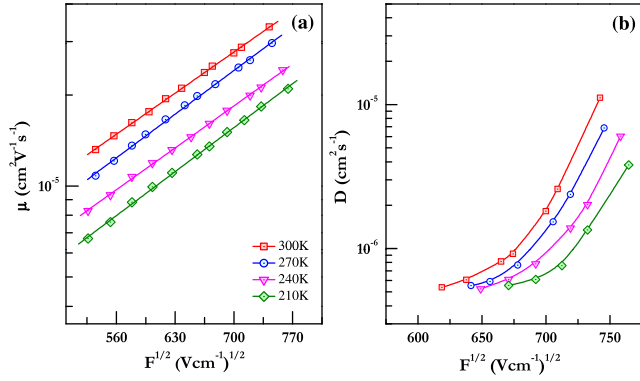


FIG. 3. Field dependence of (a) mobility and (b) diffusivity of ITO|PEDOT:PSS|PFO (65 nm)|Ca|Al device at different temperatures.

corrected for built-in potential  $V_{bi}$ . The corresponding curves for PFO are shown in Fig. 3. In each case of mobility, the slopes change with temperature as the P-F coefficient is expected to be temperature dependent.

In both cases, the most significant characteristics of  $D(F^{1/2})$  curves is that the datasets have nearly the same shape except that they are shifted linearly to higher fields for lower temperatures. For the case of Alq<sub>3</sub>, as shown in Fig. 2(b), there is a specific minimum in each of the datasets, and it is possible to shift them rigidly to match the room temperature (RT) curve by subtracting the field difference corresponding to the minimum. In doing so, all the curves fall on each other as shown in Fig. 4(a). The field dependence of diffusivity for PFO, though, is different from that observed in case of Alq<sub>3</sub>, i.e., instead of a minimum, they display a characteristic threshold in field beyond which it increases sharply (almost exponentially). The  $D(F^{1/2})$  curve can now be rigidly shifted along the field axis subtracting the relative difference in the characteristic threshold field again resulting into a collapse of all datasets into one curve as shown in Fig. 4(b). The field at which the diffusivity is minimum for Alq<sub>3</sub>, and the threshold for the case of PFO is termed as the critical field ( $F_c$ ). This empirical observation on the existence of a critical field for diffusivity for both materials is crucial to the results and discussion of this paper. For convenience of discussion, we refer the process of shifting the curve along the field axis by the critical field as “shift-normalization.” It is important to note that this

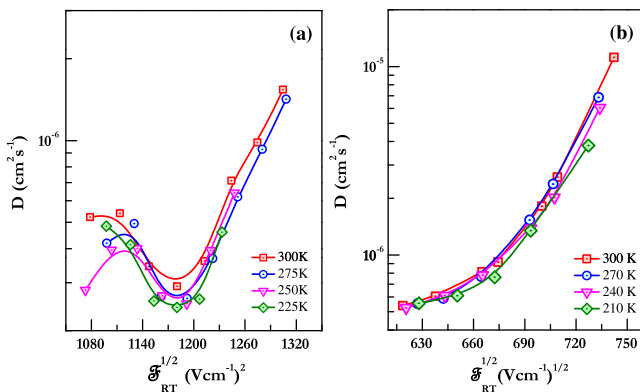


FIG. 4. Diffusivity as a function of shift-normalized field  $\mathcal{F}_{RT}$ : (a) for the Alq<sub>3</sub> and (b) for the PFO.

observation has been possible because of experimental determination of temperature dependence of carrier diffusivity in such systems.

In an early seminal paper, Richert *et al.*<sup>20</sup> studied the drift and diffusion of charge carrier in the hopping regime within the Gaussian DOS in presence of external electric field. They showed that the diffusion constant increases much more rapidly either with field or Gaussian variance than does mobility. Bouchaud and Georges<sup>27</sup> inferred these findings by suggesting an expression which predicts a linear relation between field and diffusivity in inhomogeneous system. Subsequently, Hirao *et al.*<sup>21</sup> claimed to determine the diffusivity and the mobility of molecularly doped polymers performing Monte-Carlo parameter fittings to the experimental transient photocurrent signals. However, since these fittings use TOF transients, the results relate to quasi-equilibrium conditions only. Moreover, they proposed a field and temperature dependence expression of the diffusivity analogous to the mobility relation developed within the disorder formalism. Nikitenko *et al.*<sup>13</sup> developed an analytical model to study hopping transport in non-equilibrium condition, wherein the field-assisted diffusion was found to have a quadratic field-dependence. Nenashev *et al.*<sup>23,24</sup> formulated an analytical theory to compute the field dependence of diffusivity in strongly anisotropic disordered solids with one-, two-, and three-dimensional hopping transport modes. None of the models have been verified with experimental data as yet. The field dependence of diffusivity observed in this work, conceptually in agreement with the insights of Richert *et al.*,<sup>20</sup> needs more systematic understanding in future.

### C. Critical field: Temperature dependence

We also note that the critical field in both the materials decreases linearly with temperature as shown in Fig. 5 and vanish for temperatures corresponding to a specific temperature  $T^*$  which turns out to be 455 K and 1050 K for Alq<sub>3</sub> and PFO, respectively. Hence, we can empirically write down the temperature dependence of  $F_c$  as

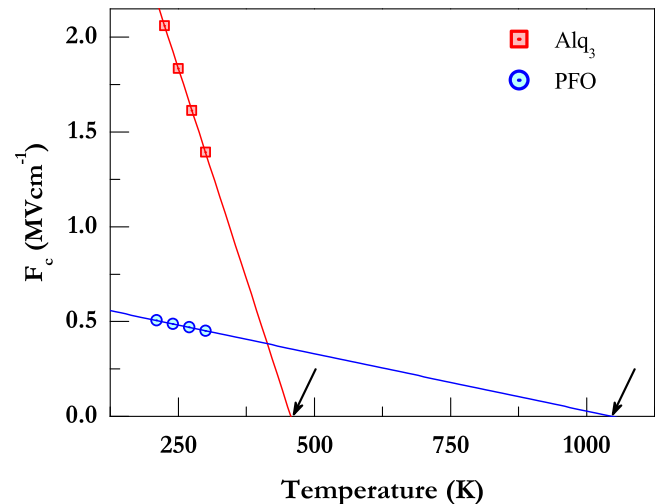


FIG. 5. The variation of critical field  $F_c$  with temperature for Alq<sub>3</sub> and PFO showing the difference in the slope and  $T^*$ , characteristic temperature at which  $F_c$  vanishes (indicated by arrows). The slope should be proportional to the average inter-site distance or localization length,  $\alpha$ .

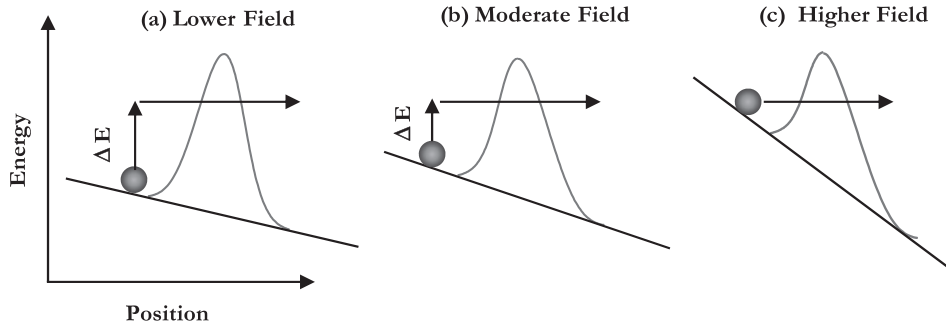


FIG. 6. Schematic illustration of thermally assisted inter-site tunneling in which field plays the role of temperature. Beyond a critical field, no assistance from temperature is needed and thus defines the high temperature limit.

$$F_c = \left( \frac{k_B}{e\alpha} \right) (T^* - T), \quad \text{for } T < T^*, \quad (3)$$

where  $\alpha$  is the localization length and  $e$  the elementary charge. We now turn to an intuitive meaning that we can associate with the occurrence of  $F_c$  at each temperature, and the high temperature limit  $T^*$  at which  $F_c$  vanishes. That high electric field can play the role of temperature for hopping conduction, was first recognized by Shklovskii,<sup>28</sup> who replaced  $T$  by an effective  $T_{eff}$  at high fields as  $T_{eff} = (eF\alpha/2k_B)$ .

The critical field can be viewed as the field beyond which the corrugations in the potential landscape are so tilted that tunneling across transport states suffices to access nearby sites, and help from thermal energy is not required. This is schematically illustrated in Fig. 6, in terms of a typical barrier between two hopping sites. This can also be represented as tilting of the DOS in energy. In other words, the carrier distribution is hot enough that relaxation in contact with localized levels is no longer important. At a sufficiently high temperature  $T^*$ , no more assistance from field is necessary for the polaron gas to become insensitive to the energy landscape. Hence, if the carrier is heated beyond a mean energy of  $k_B T^*$  (39 meV for Alq<sub>3</sub> and 90 meV for PFO), the carrier sees only spatial disorder (characterized by  $\Sigma$ ) in terms of variance in inter-site distance,  $a$ . The slope of the curves in Fig. 5 thus yields the mean localization length which turns out to be 1.4 nm for PFO and 0.1 nm for Alq<sub>3</sub>, values which agree well with those used for fitting purposes by others.<sup>6,11</sup> Clearly, small molecules are packed much closer than the polymer. The localization length can be expressed as a product of a statistical factor  $\gamma$  times the inter-site distance  $a$ . The factor  $\gamma$  has been investigated for hopping conduction in the past through detailed simulations but has been found to be a material dependent constant.<sup>29</sup> In any case, it is clear that field heating required for the case of small molecule is smaller than the polymer case since the former is more densely packed with much smaller  $\alpha$ .

We can also speculate that the need for introducing artificial characteristic temperature into fittings of mobility purely on empirical grounds in disorder solids<sup>30</sup> may be related to  $T^*$  that we obtain as an experimental result. Detailed Monte-Carlo simulations should bear out the existence of  $F_c$  and  $T^*$  in the case of transport in a Gaussian manifold. Physically, one could think of  $T^*$  as the *carrier temperature* at which field lowering of barrier is no longer required for jumps. The interplay of field and temperature in kinetic coefficients of carriers hopping in disordered

inorganic semiconductors has been studied in the past mostly for exponential DOS.<sup>29</sup> The attempt has been to try and describe transport parameters by a single effective temperature which takes into account both the effects of temperature and field.

## D. Extraction of model parameters

Taking cue from the occurrence of a characteristic or critical field using which temperature dependence of diffusivity could be annihilated through rigid translation, we also apply the same “shift-normalization” of field to mobility data. It is important to note that in carrying out shift-normalization of field for mobility, one needs more care than diffusivity. In contrast to the measurement of diffusivity, which does not involve explicit use of the value of field, mobility is obtained from the expression  $\mu = d/t_d F$ , where  $d$  is the thickness,  $t_d$  is the measured delay time, and  $F$  is the average field after  $V_{bi}$  correction. In obtaining shift-normalized mobility ( $\mu'$ ), we use the corrected field for  $F > F_c$ . In Figs. 7(a) and 7(b), we show P-F plot of  $\mu'$  after such correction with respect to RT (300 K) for both the materials, where the shift-normalized field with respect to RT is indicated as  $\mathcal{F}_{RT}^{1/2}$ . Just as in the case of diffusivity, a master curve of  $\mu'$  independent of temperature is obtained. The slope is positive since the energy variation dominates over positional disorder ( $\Sigma$ ) term in the field coefficient of Eq. (2).

Instead of using RT curve as the reference, we can get rid of all temperature dependence by simply using the shift normalized field defined as  $\mathcal{F} \equiv F - F_c > 0$  for each corresponding temperature. We obtain  $\log \mu'$  vs  $\mathcal{F}^{1/2}$  plot with

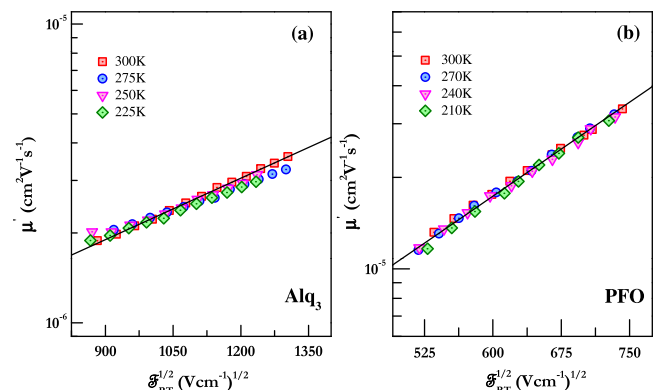


FIG. 7. Plots of  $\log \mu'$  vs  $\mathcal{F}^{1/2}$  after shift-normalization of field for both cases Alq<sub>3</sub> (a) and PFO (b) with respect to room temperature  $\mathcal{F}_{RT}$ .

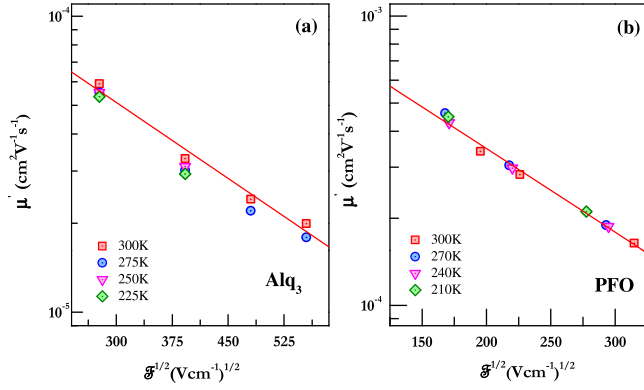


FIG. 8. Plots of  $\log \mu'$  vs  $F^{1/2}$  after shift-normalization with  $\mathcal{F} \equiv F - F_c$  for both cases Alq<sub>3</sub> (a) and PFO (b).

negative slope as shown in Figs. 8(a) and 8(b) for both the materials. This would then correspond to complete annihilation of all the temperature dependence in Eq. (2) which would correspond to the high temperature limit. The negative slope then reflects only  $\Sigma$ , and the straight line interpolates to the zero-field axis at  $\mu_{o,\infty}$  represented by  $\mu'(F) = \mu_{o,\infty} \exp(-C\Sigma^2)\sqrt{\mathcal{F}}$ . The remarkable success of this shift-normalization procedure provides a completely alternative view that for non-equilibrium carriers, the temperature dependence only shifts  $F_c$  keeping all other dependences intact as that of quasi-equilibrium. Therefore, we can now use the normalized straight lines to obtain all the parameters of GDM as given in Eq. (2). From the slope of the straight line normalized to the RT, we obtain  $C\{(\sigma/k_B T)^2 - \Sigma^2\}$ . For the straight lines corresponding to the high temperature limit, the slopes correspond to  $-C\Sigma^2$ , and their y-intercepts yield  $\mu_{o,\infty}$  and  $\sigma$ .

Taken together, this constitutes two significant achievements: (a) experimental validation of notions of GDM under non-equilibrium conditions with appropriate field scaling and (b) determination of all the parameters of GDM, including constants which are listed in Table I. A similar analysis has been carried out for CDM also, and the corresponding parameters are given in the supplemental material.<sup>26</sup> The values of the parameters are in reasonable agreement with values used in the literature.<sup>8,31–33</sup> The match of the original mobility data with the obtained parameters are shown in Figs. 9 and 10 for both GDM and CDM. In each case, a *single* multiplicative constant  $\beta$  (typically between 1 and 2) was needed to get the perfect match as shown in Figs. 9 and 10. This numerical factor can be easily incorporated into  $\mu_{o,\infty}$  and demonstrates that the value obtained is of correct order and essential robustness of the procedure. The internal

TABLE I. The parameters of GDM measured for both Alq<sub>3</sub> and PFO materials using the shift-normalization procedure.

GDM Parameters	Units	Alq <sub>3</sub>	PFO
$\mu_{o,\infty}$	$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	$1.7 \times 10^{-4}$	$1.3 \times 10^{-3}$
$C$	$\text{cm}^{1/2} \text{V}^{-1/2}$	$4.7 \times 10^{-4}$	$7.3 \times 10^{-4}$
$\sigma$	meV	90	99
$\Sigma$	Unit-less	2.9	3.0

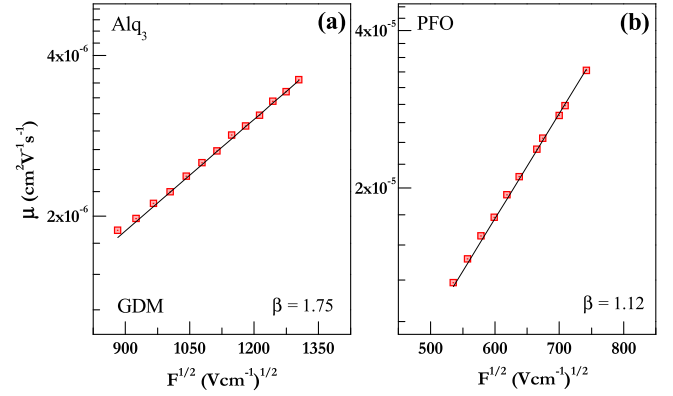


FIG. 9. Fit with GDM parameters (listed in Table I), obtained from analysis given in the text. The data fit perfectly to the mobility measured directly using a multiplicative constant indicated in the figure.

consistency of the parameters obtained is striking. We have found this procedure more reliable than the conventional analysis since possible temperature dependent drops across the device does not contribute in the process of shift-normalization. There has been a proposal that  $\mu_{o,\infty}$  could be as high as  $30 \text{ cm}^2/\text{Vs}$ ,<sup>11</sup> but the claim has been contested<sup>12</sup> as being result of invalid interpolation, and our results are in general agreement with much lower values as invoked by many authors.<sup>31–33</sup>

In a way, our results indicate that when the carrier is sufficiently hot, the mobility expressions of quasi-equilibrium become valid if proper allowance is made for the invariant scales present in the form of  $F_c$  and  $T^*$ . In that sense, hot carriers injected into the higher transport states serve as a probe to sample  $\sigma$  and  $\Sigma$  separately. In simple ELT experiments, this hot carrier regime is marked by the existence of a peak in the shape of the transient, which can be treated as a signature that carriers are hot enough to show diffusion winning over dispersion within the localized states.<sup>16</sup>

Finally, we remark that our results indeed demonstrate that diffusivity is more sensitive to disorder, and specifically its field dependence is important as has been clear from early simulations<sup>13,23–25</sup> and TOF experiments.<sup>20,21</sup> Our results show that the field dependence of diffusivity beyond  $F_c$  is

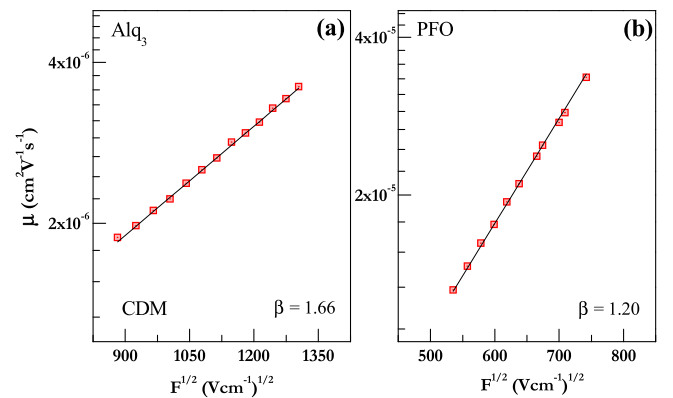


FIG. 10. Fit to the measured data using CDM parameters (listed in Table S1 in supplemental material<sup>26</sup>), obtained from analysis given in the text fits perfectly to the mobility measured directly using a multiplicative constant indicated in the figure.



nearly exponential, i.e., much stronger than linear or quadratic that is predicted by analytic theory and simulations.<sup>24</sup> The recent one dimensional theory of Nenashev *et al.* is a possible candidate,<sup>23</sup> but a detailed critical discussion on this will be reported elsewhere. The experiments and the field regime in which we describe have the potential to provide a testing ground for such theories, and our results indicate that the measurement of diffusivity would be more fruitful than mobility for such purposes.

We note that both GDM and CDM can be employed and a possible method of differentiating between the two is out of the scope of this study. The extension of our formulation to EGDM where the concentration dependence is also included is likely to yield rich dividends in terms of models and understanding. The key to further developments will be to carry out detailed simulations in the non-equilibrium regime, and their validation through carefully controlled equivalent experimental situations.

#### IV. SUMMARY AND CONCLUSIONS

In conclusion, we present temperature and field dependence of mobility and diffusivity of hot carriers in two typical disordered organic semiconductors, viz., Alq<sub>3</sub> and PFO as representative of small molecule and polymer, respectively. We discover that occurrence of a critical field beyond which diffusivity increases sharply provides a way of shift-normalizing both mobility and diffusivity to annihilate temperature dependence leading to a unified description. We use this shift-normalization procedure to completely decouple energetic and positional disorder, and independently measure all the parameters involved in GDM (or CDM). The temperature dependence of critical field yields the high temperature limit at which no assistance from field is necessary for inter-site tunneling, and the related mean localization length. Having established our procedure for different temperatures, it can now be applied to simultaneous measurements of mobility and diffusivity as a function of field at any single temperature. We provide an intuitive interpretation to highlight the physical basis of success of our heuristics, and the significance of parameters so obtained. Our experimental results pose several challenges in accommodating their implications to the current theoretical description, specifically field dependence of diffusivity, which needs more intensive experimental and simulational studies.

#### ACKNOWLEDGMENTS

We are thankful to Samtel Centre for Display Technologies, IIT Kanpur, Council of Scientific and Industrial Research, New Delhi and Department of Science

and Technology, New Delhi (DST/R&D/20060243) for financial supports.

- <sup>1</sup>H. Klauk, *Organic Electronics: Materials, Manufacturing and Applications* (Wiley-VCH, Weinheim, 2006).
- <sup>2</sup>S. Baranovski, *Charge Transport in Disordered Solids with Applications in Electronics* (John Wiley & Sons, Chichester, 2006).
- <sup>3</sup>P. M. Borsenberger, L. Pautmeier, and H. Bässler, *J. Chem. Phys.* **94**, 5447 (1991).
- <sup>4</sup>H. Bässler, *Phys. Status Solidi B* **175**, 15 (1993).
- <sup>5</sup>S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, *Phys. Rev. Lett.* **81**, 4472 (1998).
- <sup>6</sup>W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. Michels, *Phys. Rev. Lett.* **94**, 206601 (2005).
- <sup>7</sup>R. Coehoorn, W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, *Phys. Rev. B* **72**, 155206 (2005).
- <sup>8</sup>S. L. M. van Mensfoort, S. I. E. Vulto, R. A. J. Janssen, and R. Coehoorn, *Phys. Rev. B* **78**, 085208 (2008).
- <sup>9</sup>M. Bouhassoune, S. L. M. van Mensfoort, P. A. Bobbert, and R. Coehoorn, *Org. Electron.* **10**, 437 (2009).
- <sup>10</sup>A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).
- <sup>11</sup>N. I. Craciun, J. Wildeman, and P. W. M. Blom, *Phys. Rev. Lett.* **100**, 056601 (2008).
- <sup>12</sup>I. I. Fishchuk, A. K. Kadashchuk, J. Genoe, M. Ullah, H. Sitter, Th. B. Singh, N. S. Sariciftci, and H. Bässler, *Phys. Rev. B* **81**, 045202 (2010).
- <sup>13</sup>V. R. Nikitenko, H. von Seggern, and H. Bässler, *J. Phys. Condens. Matter* **19**, 136210 (2007).
- <sup>14</sup>J. Bisquert, *Phys. Chem. Chem. Phys.* **10**, 3175 (2008).
- <sup>15</sup>O. Tal, I. Epstein, O. Snir, Y. Roichman, Y. Ganot, C. K. Chan, A. Kahn, N. Tessler, and Y. Rosenwaks, *Phys. Rev. B* **77**, 201201(R) (2008).
- <sup>16</sup>A. K. Tripathi, D. C. Tripathi, and Y. N. Mohapatra, *Phys. Rev. B* **84**, 041201(R) (2011).
- <sup>17</sup>Y. Roichman and N. Tessler, *Appl. Phys. Lett.* **80**, 1948 (2002).
- <sup>18</sup>K. Harada, A. G. Werner, M. Pfeiffer, C. J. Bloom, C. M. Elliott, and K. Leo, *Phys. Rev. Lett.* **94**, 036601 (2005).
- <sup>19</sup>G. A. H. Wetzelaer, L. J. A. Koster, and P. W. M. Blom, *Phys. Rev. Lett.* **107**, 066605 (2011).
- <sup>20</sup>R. Richert, L. Pautmeier, and H. Bässler, *Phys. Rev. Lett.* **63**, 547 (1989).
- <sup>21</sup>A. Hirao, H. Nishizawa, and M. Sugiuchi, *Phys. Rev. Lett.* **75**, 1787 (1995).
- <sup>22</sup>V. Blickle, T. Speck, C. Lutz, U. Seifert, and C. Bechinger, *Phys. Rev. Lett.* **98**, 210601 (2007).
- <sup>23</sup>A. V. Nenashev, F. Jansson, S. D. Baranovskii, R. Österbacka, A. V. Dvurechenskii, and F. Gebhard, *Phys. Rev. B* **81**, 115203 (2010).
- <sup>24</sup>A. V. Nenashev, F. Jansson, S. D. Baranovskii, R. Österbacka, A. V. Dvurechenskii, and F. Gebhard, *Phys. Rev. B* **81**, 115204 (2010).
- <sup>25</sup>V. R. Nikitenko and H. von Seggern, *J. Appl. Phys.* **102**, 103708 (2007).
- <sup>26</sup>See supplemental material at <http://dx.doi.org/10.1063/1.4824747> for transport parameters determination, field correction, transport parameters extraction, and a table of extracted CDM parameters.
- <sup>27</sup>J. P. Bouchaud and A. Georges, *Phys. Rev. Lett.* **63**, 2692 (1989).
- <sup>28</sup>B. I. Shklovskii, *Sov. Phys. Semicond.* **6**, 1964 (1973).
- <sup>29</sup>B. Cleve, B. Hartenstein, S. D. Baranovskii, M. Scheidler, P. Thomas, and H. Baessler, *Phys. Rev. B* **51**, 16705 (1995).
- <sup>30</sup>W. D. Gill, *J. Appl. Phys.* **43**, 5033 (1972).
- <sup>31</sup>R. U. A. Khan, D. Poplavskyy, T. Kreouzis, and D. D. C. Bradley, *Phys. Rev. B* **75**, 035215 (2007).
- <sup>32</sup>R. J. de Vries, S. L. M. van Mensfoort, V. Shabro, S. I. E. Vulto, R. A. J. Janssen, and R. Coehoorn, *Appl. Phys. Lett.* **94**, 163307 (2009).
- <sup>33</sup>S. L. M. van Mensfoort, R. J. de Vries, V. Shabro, H. P. Loebl, R. A. J. Janssen, and R. Coehoorn, *Org. Electron.* **11**, 1408 (2010).