Universal Einstein Relation Model in Disordered Organic Semiconductors under Quasi-equilibrium

Ling Li, Nianduan Lu, and Ming Liu
(Dated: October 11, 2013)

It is still under debate whether the classical Einstein relation in disordered organic semiconductors is valid. We investigated Einstein relation in disordered organic semiconductors theoretically. The results show that, the classical Einstein relation deviate dramatically with disorder and electric field, even in the case of thermal equilibrium.

PACS numbers: 72.20.Ee, 72.80.Le, 73.61.Ph

Electron transfer and transport between organic molecules are the fundamental issue of disordered organic semiconductors. Unlike nearly perfect crystals, charge transport in amorphous and polycrystalline thin films is dominated by various kinds of defects. charge transport can be described in terms of variable-range hopping, where the charges hop from site defect to site defect, the probability of each hop depending on the site-energies and the hopping distance. These physical properties deviate significantly from classical semiconductor models. Therefore, the vaility of the Einstein relation to disordered semiconductors has been a matter of intensive research. General speaking, the Einstein relation is the relation between two fundamental transport parameters, the diffusion coefficient $D$ and the mobility $\mu$ of charge carriers, which reads as [1]

$$D = \frac{k_B T}{\mu q}$$

(1)

with $k_B$ the Boltzmann constant, $T$ the temperature, and $q$ the elementary charge. Numerous theoretical and experimental studies concluded that the Einstein relation is violated under non-equilibrium conditions, mainly due to the electric field dependence of the diffusivity being larger than the field response of the mobility.

However, because of large disorder, charge transport in an organic molecular crystal, being a sequence of transfers of an excess charge on one molecule to one of its neighboring molecules, is a relatively slow process and the time for carriers to equilibrate can be very large, so that non-equilibrium transport is maybe not uncommon in disordered semiconductors. Under quasiequilibrium conditions, it has been proposed that, the more general Einstein relation should be written as [3–10]

$$\frac{D}{\mu} = \frac{p}{q \partial p / \partial E_F}.$$  

(2)

Where $E_F$ is the Fermi-level and $p$ is the carrier concentration relating to the density of states (DOS) as

$$p = \int \frac{g(E)}{1 + \exp \left( \frac{E - E_F}{k_B T} \right)} dE.$$  

(3)

As a result, the Einstein relation becomes charge-density- and temperature-dependent. However, the Einstein relation, defined as equation (2), is till under suspicion. Even though such a derivation is commonly accepted, Baranovskii et al. mentioned that equation (2) is valid only when $\mu$ and $D$ are considered independent of energy, which is not the case for hopping transport or relaxation in an exponential band tail. Moreover, the detailed hopping transport information, for example, electric field and lattice spacing has never been addressed in equation (2).

In this letter, we present here a universal model for Einstein relation in disordered organic semiconductors under quasi-equilibrium condition. The effect of the electric field, temperature, and carrier concentration on the Einstein relation are well addressed.

Model.—In general, the basis for models describing the charge transport in disordered semiconductors is Miller-Abrahams expressions, where the hopping transport takes place via tunneling between an initial state $i$ and a target state $j$. The tunneling process is described by

$$\nu = \nu_0 \exp (-u) = \nu_0 \begin{cases} \exp \left( -2 \alpha R_{ij} - \frac{E_i - E_j}{k_B T} \right), & E_i > E_j \\ (-2 \alpha R_{ij}), & E_i < E_j \end{cases}$$

(4)

As a result, the electron transfer and transport between organic molecules are the fundamental issue of disordered organic semiconductors. Unlike nearly perfect crystals, charge transport in amorphous and polycrystalline thin films is dominated by various kinds of defects. charge transport can be described in terms of variable-range hopping, where the charges hop from site defect to site defect, the probability of each hop depending on the site-energies and the hopping distance. These physical properties deviate significantly from classical semiconductor models. Therefore, the validity of the Einstein relation to disordered semiconductors has been a matter of intensive research. General speaking, the Einstein relation is the relation between two fundamental transport parameters, the diffusion coefficient $D$ and the mobility $\mu$ of charge carriers, which reads as [1]

$$D = \frac{k_B T}{\mu q}$$

(1)

with $k_B$ the Boltzmann constant, $T$ the temperature, and $q$ the elementary charge. Numerous theoretical and experimental studies concluded that the Einstein relation is violated under non-equilibrium conditions, mainly due to the electric field dependence of the diffusivity being larger than the field response of the mobility.

However, because of large disorder, charge transport in an organic molecular crystal, being a sequence of transfers of an excess charge on one molecule to one of its neighboring molecules, is a relatively slow process and the time for carriers to equilibrate can be very large, so that non-equilibrium transport is maybe not uncommon in disordered semiconductors. Under quasi-equilibrium conditions, it has been proposed that, the more general Einstein relation should be written as [3–10]

$$\frac{D}{\mu} = \frac{p}{q \partial p / \partial E_F}.$$  

(2)

Where $E_F$ is the Fermi-level and $p$ is the carrier concentration relating to the density of states (DOS) as

$$p = \int \frac{g(E)}{1 + \exp \left( \frac{E - E_F}{k_B T} \right)} dE.$$  

(3)

As a result, the Einstein relation becomes charge-density- and temperature-dependent. However, the Einstein relation, defined as equation (2), is till under suspicion. Even though such a derivation is commonly accepted, Baranovskii et al. mentioned that equation (2) is valid only when $\mu$ and $D$ are considered independent of energy, which is not the case for hopping transport or relaxation in an exponential band tail. Moreover, the detailed hopping transport information, for example, electric field and lattice spacing has never been addressed in equation (2).

In this letter, we present here a universal model for Einstein relation in disordered organic semiconductors under quasi-equilibrium condition. The effect of the electric field, temperature, and carrier concentration on the Einstein relation are well addressed.

Model.—In general, the basis for models describing the charge transport in disordered semiconductors is Miller-Abrahams expressions, where the hopping transport takes place via tunneling between an initial state $i$ and a target state $j$. The tunneling process is described by

$$\nu = \nu_0 \exp (-u) = \nu_0 \begin{cases} \exp \left( -2 \alpha R_{ij} - \frac{E_i - E_j}{k_B T} \right), & E_i > E_j \\ (-2 \alpha R_{ij}), & E_i < E_j \end{cases}$$

(4)

Here, $\nu_0$ is the attempt-to-jump frequency, $R_{ij}$ is the hopping distance, $u$ is the hopping range, $E_i$ and $E_j$ are the energies at sites $i$ and $j$, respectively, and $\alpha$ is the inverse localized length. However, in real organic semiconductor systems, when an electric field $F$ exists, this electric field will lower the Coulomb barrier, which leads to a reduction in the thermal activation energies, and the hopping range with normalized energy ($\epsilon = E/k_B T$) can
therefore be rewritten as \[15,17\]

\[ u = \begin{cases} 
2 \alpha (1 + \beta \cos \theta) R_{ij} + \epsilon_j - \epsilon_i, & \epsilon_j > \epsilon_i - \beta \cos \theta \\
2 \alpha R_{ij}.
\end{cases} \tag{5} \]

where \( \beta = F e/2 \alpha k_B T \) and \( \theta \) is the angle between \( R_{ij} \) and the electric field ranging from 0 to \( \pi \). For a site with energy \( \epsilon_i \) in the hopping space, the most probable hop for a carrier on this site is to an empty site at a range \( u \), for which it needs the minimum energy. The conduction is a result of a long sequence of hops through this hopping space. For simplicity, one-dimensional charge transport is taken at first. In this situation, the average hopping range \( R_{nn} \) can be obtained following the approach used in our previous work \[17\], the average hopping distance along the electric field, \( \bar{x}_f \) is given as

\[ \bar{x}_f = \frac{I_1 + I_2}{I_3 + I_4} \tag{6} \]

where

\[ I_1 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) \frac{R_{nn} - \epsilon_i + \epsilon}{1 \pm \beta} x d\epsilon \]

\[ I_2 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) R_{nn} x d\epsilon \]

\[ I_3 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) \frac{R_{nn} - \epsilon_i + \epsilon}{1 \pm \beta} d\epsilon \]

\[ I_4 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) R_{nn} x d\epsilon \]

The mobility at energy \( \epsilon_i \) is

\[ \mu(\epsilon_i) = \lim_{t \to \infty} \frac{\partial x_f}{\partial t} = \frac{\nu_0 \bar{x}_f}{F} \exp(\beta \mu). \tag{7} \]

Where \( g(\epsilon) \) is the density of states, and \( f(\epsilon_i, \mu) = 1/(1 + \exp(\epsilon_i - \mu)) \) is the Fermi-Dirac distribution with \( \mu \) denoting the Fermi level. We take the Gaussian form of \( g(\epsilon) = \frac{N_0}{\sqrt{\pi \sigma^2_0}} \exp\left(-\frac{\epsilon^2}{2\sigma^2_0}\right) \) as the DOS in the full manuscript, where \( N_0 \) is the number of states per unit volume and \( \sigma_0 = \sigma/k_B T \) indicates the width of the DOS. \( N_0 = 1 \times 10^{28} m^{-3} \) is used in the full manuscript as a typical value for the relevant organic semiconductor.

On the other hand, to calculate the diffusion constant \( D \), we shall use the following definitions

\[ D(\epsilon_i) = \frac{1}{2} \lim_{t \to \infty} \frac{d}{dt} \left[ \frac{x_f^2}{2} - \bar{x}_f^2 \right] = \frac{\left[ x_f^2 - \bar{x}_f^2 \right]}{2} \times \nu_0 R_{nn} \exp(-\beta \mu). \]

The average the mean squared displacement of the carriers \( x_f^2 \) should be calculated as

\[ x_f^2 = \frac{I'_1 + I'_2}{I'_3 + I'_4} \tag{8} \]

where

\[ I'_1 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) \frac{R_{nn} - \epsilon_i + \epsilon}{1 \pm \beta} x d\epsilon \]

\[ I'_2 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) R_{nn} x d\epsilon \]

\[ I'_3 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) \frac{R_{nn} - \epsilon_i + \epsilon}{1 \pm \beta} d\epsilon \]

\[ I'_4 = \sum \int_{\epsilon_i \pm R_{nn}}^{\epsilon_i + R_{nn}} g(\epsilon) (1 - f(\epsilon, \mu)) R_{nn} x d\epsilon \]

\[ D(\epsilon_i) = \frac{\bar{R}_f^2 - \bar{x}_f^2}{2\bar{x}_f} \tag{9} \]

The Einstein relation in the hopping system can reasonably formulated as

\[ D = \frac{\int_{-\infty}^{\infty} E(\epsilon) g(\epsilon) (1 - f(\epsilon, \mu)) d\epsilon}{\int_{-\infty}^{\infty} g(\epsilon) (1 - f(\epsilon, \mu)) d\epsilon} \tag{10} \]

To test the validity of Einstein relation, in Fig. 1, we firstly plot the energy dependent of \( E(\epsilon) \), using equation (9). The parameters chosen here are typical ones for organic semiconductors as: \( F = 1 \times 10^8 V/m, \alpha^{-1} = 1 nm, \)
large energy disorder, as demonstrated clearly in Fig. 2. In this situation, $eD/\mu k_B T$ is as high as two times of unity, even at high temperature and deep energy. Physically, since the hopping rate is actually energy dependent, mobility or diffusion is therefore dependent on the energy; Moreover, it has been pointed out that the energy dependent transport in amorphous materials is more closely related to diffusivity than mobility, $eD/\mu k_B T$ will deviate from unity more rapidly at higher energies [18–20]. Figures 3 and 4 quantifies the deviation of overall $eD/\mu k_B T$ (equation 10) from the classic Einstein relation by showing how $eD/\mu k_B T$ varies with the degree of disorder, temperature, and electric field. The results are similar to the $eD/\mu k_B T$ in non-equilibrium transport, where the deviation increases with material disorder and electric field, while decreases with temperature.

Physical origin related to this deviation is similar to the non-equilibrium as well, in energy or positional disorder circumananal, the carrier predetermined paths defined by highest exchange frequencies will govern carrier motion with certain configurations being likely to override the tendency of a carrier to follow the biasing field. The larger disorder, the more deviation.

Another interesting feature appears when plotting $eD/\mu k_B T$ as a function of the carrier concentration, as depicted in the inset of Fig. 5. $eD/\mu k_B T$ here is found weakly dependent on carrier concentration and decrease with concentration finally, which is in contrast to the predictions based on equation (2)[3]. To explain the above results we examine in Fig. 5 the carrier concentration dependencies of both the diffusivity $D$ and mobility $\mu$ of the charge carriers for $\sigma/k_B T = 3.8$.

Apparently, both $D$ and $\mu$ increases with carrier concentration. Remarkably, however, the diffusivity increases nearly the same rapidly with carrier concentration as does $\mu$. The constant deviations is speculated from the temperature and material disorder.

The question now coming out is whether these results are consistent with the experimental data. The two available data for the quasi-equilibrium regime are those of blom et al. [21] and keo et.al. [22]. These data were obtained by measuring the ideality factor in single carrier organic diode. It is well seen in Fig. 3 that the relation between $D$ and $\mu$ differs from the Einstein’s formula dramatically, which agree with the observation in [22]. However, it has been argued that deviation of Einstein relation in [22] is an experimental artifact that is caused by a too large leakage current [21]. Therefore, the comparison is not shown here.

It should be noted that, based on our calculation, the Einstein relation is strongly dependent on material disorder, temperature, and electric field, let $f(F, \sigma, T) =$
In diffusion theory, drift and diffusion current $J$ of the M-i-n diode reads as

$$J = n\mu \frac{\partial V}{\partial x} + D \frac{\partial n}{\partial x}. \quad (11)$$

Following the classical derivation [], an integrating factor $\exp \left( -\frac{qV}{f(T,F,\sigma)} \right)$ is used to integrate equation (11) over the $i$ layer ranging from $x = 0$ to $x = W$:

$$J \int_0^W \exp \left( -\frac{qV}{f(T,F,\sigma)} \right) dx \neq \mu f(T,F,\sigma) \times n \exp \left( -\frac{qV}{f(T,F,\sigma)} \right) \quad (12)$$

Hence we conclude that the measured ideality factor cannot be used to prove or disprove the validity of the generalized Einstein relation. This idea clearly calls for rigorous experimental work which we hope this Letter will stimulate.

In conclusion, the universal model of the Einstein relation in disordered organic semiconductors has been proposed here based on variable range hopping theory. In contrast to earlier experimental reports, deviation of $eD/\mu k_B T$ from unity is obtained. Furthermore, it is found here $eD/\mu k_B T$ is actually weakly dependent on carrier concentration, which is in contradiction with the generalized Einstein relation derived for a Gaussian DOS.

Furthermore, the valid of measuring ideality factor to check Einstein relation is also discussed.

Financial support from NSFC (No. 60825403) and National 973 Program 2011CB808404 is acknowledged.

* Electronic address: lingli@ime.ac.cn, liuming@ime.ac.cn

Institute of Microelectronics, Chinese Academy of Sciences, Beijing, 100029, China

[1] A. Einstein, Ann. Phys. (Leipzig) 322, 549 (1905).
[2] R. Richert, L. Pautmeier, and H. Bassler, Phys. Rev. Lett. 63, 547 (1989).
[3] P. M. Borsenberger, L. Pautmeier, R. Richert, and H. Bassler, J. Chem. Phys. 94, 8276 (1991).
[4] S. D. Baranovskii, T. Faber, F. Hensel, P. Thomas, and G. J. Adriaenssens, J. Non-Cryst. Solids 198C200, 214 (1996).
[5] J. P. Bouchaud, and A. Georges, Phys. Rev. Lett. 63,2692 (1989).
[6] Stijn Verlaak, and Paul Heremans, Phys. Rev. B. 75, 115127 (2007).
[7] S. Verlaak, C. Rolin, and P. Heremans, J. Phys. Chem. B. 111, 139 (2007).
[8] W. Ashcroft and N. D. Mermin, Solid State Physics Holt, Rinehart and Winston, New York, 1988.
[9] Y. Roichman and N. Tessler, Appl. Phys. Lett. 80, 1948 (2002).
[10] L. Li, G. Meller, and H. Kosina, J. Appl. Phys. 106, 013714 (2009).
[11] A.V. Nenashev, F. Jansson, S. D. Baranovskii, R. Osterbacka, A.V. Dvurechenskii, and F. Gebhard, Phys. Rev. B 81, 115204 (2010).
[12] H. Bassler, Phys. Status Solidi B Res. A 175, 15 (1993).
[13] H. Bassler, Phys. Status Solidi B Res. A 107, 9 (1981).
[14] A. Miller, and E. Abraham, Phys. Rev. B 120, 745 (1960).
[15] N. Apsley, and H. P. Hughes, Philos. Mag. 31, 1327 (1975).
[16] V. I. Arkhipov, E. V. Emelianova, and G. J. Adriaenssens, Phys. Rev. B 64, 985 (2001), 125125(2001).
[17] L. Li, S. Winckel, J. Genoe, and P. Heremans, Appl. Phys. Lett. 95 153301 (2009).
[18] P. N. Butcher, J. Phys. C. 5,3164 (1972).
[19] N. F. Mott, J. Phys. C 20, 3075 (1987).
[20] N.F.Mott, Phil.Mag. 19 835-52 (1969).
[21] G. A. H. Wetzelaer, L. J. A. Koster, and P.W. M. Blom, Phys. Rev. Lett. 107, 066605 (2011).
[22] K. Harada, A. G. Werner, M. Pfeiffer, C. J. Bloom, C. M. Elliott, and K. Leo, Phys. Rev. Lett. 94, 036601 (2005).