General Einstein relation model in disordered organic semiconductors under quasiequilibrium

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In this work, the Einstein relation between the diffusivity and mobility of charge carriers for disordered organic semiconductors is analyzed. We formulate an analytic theory that allows predicting the Einstein relation for charge carrier hopping in disordered organic semiconductors with Gaussian density of states distribution as a function of disorder, temperature, bias field, and Fermi level, i.e., concentration of occupied states of the DOS under the condition of quasiequilibrium. By scanning the Fermi across the DOS, we calculate the charge carrier mobility and diffusivity as well the $qD/\mu k_BT$ ratio. We are thus able to identify the role of mobile and localized states on the interplay of diffusion and drift and can determine under which condition Einstein relation is valid or not.

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I. INTRODUCTION

Charge transport is a fundamental issue of disordered organic semiconductors. Unlike in nearly perfect crystals, charge transport in amorphous and polycrystalline thin films is dominated by various kinds of defects. Charge transport is usually described in terms of variable-range hopping, where the charges hop from site defect to site defect, where the probability of each hop depends on the site energy and the hopping distance. Therefore the transport mechanism deviates significantly from what classical semiconductor models predict and the validity of the Einstein relation is open to conjecture [1,2]. Generally speaking, the Einstein relation is the relation between two fundamental transport parameters, i.e., the diffusion coefficient of charge carriers D and their mobility μ, and reads as [3]

$$\frac{D}{\mu} = \frac{k_B T}{q}, \tag{1}$$

with k_B the Boltzmann constant, T the temperature, and q the elementary charge. Numerous theoretical and experimental studies [4–7] indicate, however, that in the presence of disorder the Einstein relation can be violated. For nonequilibrium transport, it shows that there is a disorder driven anomalous spreading of a charge carrier packet in the presence of an electric field with the coefficient for anomalous diffusion increasing quadratically with electric field [8–10]. Meanwhile, the theory for rationalizing the interplay between diffusion and drift of charge carriers in a semiconductor has been extended to include the dependence of the carrier concentration under the premise of quasiequilibrium conditions. It has been proposed that a more general Einstein relation should read as [11–13]

$$\frac{D}{\mu} = \frac{n}{q\partial n/\partial E_F}, \tag{2}$$

where E_F is the quasi-Fermi-level and n is the carrier concentration in the DOS,

$$n = \int_{-\infty}^{\infty} \frac{g(E)}{1+\exp\left(\frac{E-E_F}{k_BT}\right)} dE. \tag{3}$$

Equation (2) predicts that D/μ should increase with increasing charge density [11]. However, Eq. (2) is derived under the condition that in the continuity equation, drift and diffusion of charge carriers at the Fermi level of a semiconductor are exactly compensated. This implies that there is no net current and Eq. (2) therefore is only valid under small perturbations from equilibrium, i.e., at low electric fields where the conduction is ohmic. In an organic semiconductor diode or in a field effect transistor this condition will be violated. Moreover, Eq. (2) does not consider that charge transport occurs in a rough energy landscape. Applying Eq. (2) to such system is, therefore, an arguable procedure. In fact, recent analyses of Einstein ratio based upon the current-voltage dependence on an organic diode are controversial [1,2]. From Monte Carlo simulations, Mendels and Tessler [14] conclude that the Einstein ratio remains at the classic value of $qD/\mu k_BT = 1$, independent of the charge carrier concentration. This is at variance with both Eq. (2) and time of flight studies on charge transport that feature long tails.

Considering these controversies we developed a general model for the Einstein ratio as a function of electric field, temperature, and, notably, on charge carrier concentration applied to either one- or three-dimensional disordered organic semiconductors under the premise of quasiequilibrium. It will show under which conditions $qD/\mu k_BT$ will deviate from unity.

II. MODEL

Models for describing the charge transport in disordered semiconductors are usually based upon the Miller-Abrahams formalism for the jump rate [15]. It is appropriate for charge carriers hopping at moderate temperatures [16], and assumes that hopping transport takes place via tunneling between an initial state i and a target state j with a rate

$$\begin{aligned} \nu &= \nu_0 \exp(-R) \\ &= \nu_0 \begin{cases} \exp\left(-2\alpha R_{ij} - \frac{E_j - E_i}{k_BT}\right), & E_i < E_j \\ \exp(-2\alpha R_{ij}). & E_i > E_j \end{cases} . \end{aligned} \tag{4}$$

Here, ν_0 is the attempt-to-jump frequency, R_{ij} is the hopping distance, R is the hopping range [17–19], E_i and E_j are the energies at sites i and j, respectively, and α is the inverse

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localized length. An applied electric field will reduce the activation energy for upward jumps in field direction. The hopping range with normalized coordinates ($\epsilon = E/k_BT$ and $r_{ij} = 2\alpha R_{ij}$) can therefore be rewritten as [17,20]

$$R = \begin{cases} (1+\beta\cos\theta)r_{ij} + \epsilon_j - \epsilon_i, & \epsilon_j > \epsilon_i - \beta\cos\theta r_{ij} \\ r_{ij}, & \epsilon_j < \epsilon_i - \beta\cos\theta r_{ij} \end{cases}, \tag{5}$$

where $\beta = Fq/2\alpha k_BT$ and θ is the angle between R_{ij} and the electric field ranging from 0 to π. For a site with energy ϵ_i in hopping space, the most probable hop for a carrier on this site is to an empty site at a range R, under the condition that energy be minimized. Transport is a result of a series of hops through this hopping space. So the mobility (diffusivity) will depend on an average of the probabilities of sequential tunneling events under quasiequilibrium (see Appendix A). For simplicity, one-dimensional (1D) charge transport will be considered first. The average hopping range R_{nn} can be obtained from the approach used our previous work [20] by solving equation

$$B_c = \frac{1}{2\alpha}\int_0^{R_{nn}}\int_{-\infty}^{R_{nn}+\epsilon_i - r_{ij}(1\pm\beta)} \tau(\epsilon,\epsilon_F)d\epsilon dr_{ij}.$$

Where $B_c \approx 1$ is the percolation criterion for a one-dimensional system [21], $g(\epsilon)$ is the density of states, and $\tau(\epsilon,\epsilon_F) = g(\epsilon)[1 - f(\epsilon,\epsilon_F)]$ with $f(\epsilon,\epsilon_F) = 1/[1+\exp(\epsilon - \epsilon_F)]$ being the Fermi-Dirac distribution. Here, we consider a one-dimensional Gaussian-shaped DOS of the form of $g(\epsilon) = \frac{N_t}{\sqrt{2\pi}\sigma_0}\exp(-\frac{\epsilon^2}{2\sigma_0^2})$ [22,23], where N_t is the number of states per unit length, typical $1 \times 10^9\ \mathrm{m}^{-1}$, and $\sigma_0 = \sigma/k_BT$. Most of the calculations were done for the case of weak disorder, $\sigma/k_BT \leqslant 3$, where dispersion effects are negligible. In order to study transport as a function of the concentration of charge carriers, the DOS distribution will be filled up to a variable Fermi level.

Generally speaking, the Einstein relation can be calculated by using the following definition:

$$\frac{D}{\mu} = \frac{(\bar{x^2} - \bar{x}^2)/2^d t}{\bar{x}/Ft} = \frac{F(\bar{x^2} - \bar{x}^2)}{2^d\bar{x}},$$

where x is the position of carrier, t is time, and d is the dimensionality. At zero electric field, a particle with energy ϵ_i at a given site hops over a distance R_{nn} in the hopping space. Because these hops occur in random directions, there will be, on average, no net spatial displacement. In the presence, there is a prevalence of jumps along the field direction and, concomitantly, there will be a net displacement. Summing up the jumps trajectories for an initial energy ϵ_i, 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

$$I_1 = \sum\nolimits_\pm \int_{\epsilon_i \pm\beta R_{nn}}^{\epsilon_i + R_{nn}} \tau(\epsilon,\epsilon_F)\left(\frac{R_{nn} - \epsilon_i + \epsilon}{1\pm\beta}\right)d\epsilon,$$

$$I_2 = \sum\nolimits_\pm \int_{-\infty}^{\epsilon_i\pm\beta R_{nn}} \tau(\epsilon,\epsilon_F)R_{nn}d\epsilon,$$

$$I_3 = \sum\nolimits_\pm \int_{\epsilon_i\pm\beta R_{nn}}^{\epsilon_i + R_{nn}} \tau(\epsilon,\epsilon_F)d\epsilon,$$

$$I_4 = \sum\nolimits_\pm \int_{-\infty}^{\epsilon_i\pm\beta R_{nn}} \tau(\epsilon,\epsilon_F)d\epsilon.$$

In the hopping space, the probability of all these hops is $\exp(-R_{nn})$. Knowing the average hopping distance allows calculating the average rate of the transport, i.e., is $\nu_0\bar{x}_f\exp(-R_{nn})$. Hence the mobility at energy ϵ_i is

$$\mu(\epsilon_i) = \lim_{t\to\infty}\frac{d\bar{x}_f}{Fdt} = \frac{\nu_0\bar{x}_f}{F}\exp(-R_{nn}). \tag{7}$$

To calculate the diffusion constant D in the long-time limit, we shall use the definition

$$\begin{aligned} D(\epsilon_i) &= \frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}[\bar{x_f^2} - \bar{x_f}^2] \\ &= \frac{[(\bar{x_f}+\Delta x)^2 - \bar{x_f}^2]}{2}\nu_0\exp(-R_{nn}) \\ &= \frac{[(\bar{x_f} + \nu_0\exp(-R_{nn})t(\epsilon))^2 - \bar{x_f}^2]}{2}\nu_0\exp(-R_{nn}). \end{aligned}$$

The term of $t(\epsilon)$ in the expression appears due to the stochastic variance of times of carrier release from deep traps, written as

$$t(\epsilon) = \frac{I_1' + I_2'}{I_3' + I_4'}, \tag{8}$$

where

$$\begin{aligned} I_1' &= \sum\nolimits_\pm \int_0^{R_{nn}} dr \int_{\epsilon_i\pm\beta R_{ij}}^{\epsilon_i + r} d\epsilon \frac{\tau(\epsilon,\epsilon_F)}{\nu_0} \\ &\quad \times \exp(2\alpha(1\pm\beta)r + \epsilon - \epsilon_i), \\ I_2' &= \sum\nolimits_\pm \int_0^{R_{nn}} dr \int_{-\infty}^{\epsilon_i\pm\beta r} d\epsilon \frac{\tau(\epsilon,\epsilon_F)}{\nu_0}\exp(2\alpha(1\pm\beta)r), \\ I_3' &= \sum\nolimits_\pm \int_0^{R_{nn}} dr \int_{\epsilon_i\pm\beta r}^{\epsilon_i + r} d\epsilon\tau(\epsilon,\epsilon_F)d\epsilon, \\ I_4' &= \sum\nolimits_\pm \int_0^{R_{nn}} dR_{ij} \int_{-\infty}^{\epsilon_i\pm\beta r} d\epsilon\tau(\epsilon,\epsilon_F). \end{aligned}$$

This yields the Einstein relation as a function of the normalized site energy ϵ_i:

$$\frac{D(\epsilon_i)}{\mu(\epsilon_i)} = \frac{F\left[\bar{x_f^2} - \bar{x_f}^2\right]}{2\bar{x_f}}. \tag{9}$$

After averaging over the normalized site energies, we end up with

$$\frac{D}{\mu} = \frac{\int_{-\infty}^{\infty} d\epsilon \frac{D(\epsilon_i)}{\mu(\epsilon_i)} g(\epsilon_i) f(\epsilon_i,\epsilon_F)}{\int_{-\infty}^{\infty} d\epsilon g(\epsilon_i) f(\epsilon_i,\epsilon_F)}. \tag{10}$$

D/μ depends on normalized disorder and electric field because both D and μ depend differently on electric, temperature, and degree of disorder [25].

Using a similar way, we extend the results for the 1D calculation to a three-dimensional (3D) network of hopping sites. In this situation, the values of R_{nn} can be determined from

$$B_c = \frac{1}{8\alpha^3}\int_0^{\pi} d\theta \sin\theta \int_0^{R_{nn}} dr_{ij} 2\pi r_{ij}^2 \times \int_{-\infty}^{R_{nn}+\epsilon_i - r_{ij}(1+\beta\cos\theta)} d\epsilon \tau(\epsilon,\epsilon_F).$$

Here, $B_c = 2.8$ [24] and I_1-I_4' can be presented as

$$I_1 = \int_0^{\pi} d\theta \sin\theta \int_{\epsilon_i - \beta R_{nn}\cos\theta}^{\epsilon_i + R_{nn}} d\epsilon \tau(\epsilon,\epsilon_F)\left(\frac{R_{nn}-\epsilon+\epsilon_i}{1+\beta\cos\theta}\right)^3 \times \cos\theta,$$

$$I_2 = \int_0^{\pi} d\theta \sin\theta \int_{-\infty}^{\epsilon_i - \beta R_{nn}\cos\theta} d\epsilon \tau(\epsilon,\epsilon_F) R_{nn}^3 \cos\theta,$$

$$I_3 = \int_0^{\pi} d\theta \sin\theta \int_{\epsilon_i - \beta R_{nn}\cos\theta}^{\epsilon_i + R_{nn}} d\epsilon \tau(\epsilon,\epsilon_F)\left(\frac{R_{nn}-\epsilon+\epsilon_i}{1+\beta\cos\theta}\right)^2,$$

$$I_4 = \int_0^{\pi} d\theta \sin\theta \int_{-\infty}^{\epsilon_i - \beta R_{nn}\cos\theta} d\epsilon \tau(\epsilon,\epsilon_F) R_{nn}^2,$$

$$I_1' = \int_0^{\pi} d\theta \sin\theta \int_0^{R_{nn}} dr 2\pi r^2 \int_{\epsilon_i - r\beta\cos\theta}^{R_{nn}+\epsilon_i - r(1+\beta\cos\theta)} d\epsilon \times \frac{\tau(\epsilon,\epsilon_F)}{\nu_0}\exp(2\alpha(1+\beta\cos\theta)r + \epsilon - \epsilon_i),$$

$$I_2' = \int_0^{\pi} d\theta \sin\theta \int_0^{R_{nn}} dr 2\pi r^2 \int_{-\infty}^{\epsilon_i - r\beta\cos\theta} d\epsilon \frac{\tau(\epsilon,\epsilon_F)}{\nu_0} \times \exp(2\alpha(1+\beta\cos\theta)r),$$

$$I_3' = \int_0^{\pi} d\theta \sin\theta \int_0^{R_{nn}} dr 2\pi r^2 \int_{\epsilon_i - r\beta\cos\theta}^{R_{nn}+\epsilon_i - r(1+\beta\cos\theta)} d\epsilon \tau(\epsilon,\epsilon_F),$$

$$I_4' = \int_0^{\pi} d\theta \sin\theta \int_0^{R_{nn}} dr 2\pi r^2 \int_{-\infty}^{\epsilon_i - r\beta\cos\theta} d\epsilon \tau(\epsilon,\epsilon_F).$$

Substituting I_1-I_4' into Eqs. (6) and (8), the Einstein relation at energy ϵ_i in three-dimensional space can be calculated by

$$\frac{D(\epsilon_i)}{\mu(\epsilon_i)} = \frac{F\left[\bar{x_f^2} - \bar{x_f}^2\right]}{6\bar{x_f}}. \tag{11}$$

Connecting Eqs. (10) and (11), one obtains the Einstein relation in the three-dimensional case.

III. RESULTS AND DISCUSSION

In Fig. 1, we first show the dependence of $qD/\mu k_BT$ as a function of the disorder parameter σ/k_BT for a 3D system with a localization radius $\alpha^{-1} = 1$ nm and an electric field $F = 1\times 10^7$ V/m, parametric in the position of the Fermi level E_F. $qD/\mu k_BT$ approaches an exponential dependence on $(\sigma/k_BT)^2$. This type of dependence on the disorder parameter is a characteristic feature of hopping transport within a Gaussian DOS. It is a signature of the fact that in a virtually empty DOS charge carriers tend to equilibrate at an average energy of $E_\infty/\sigma = \sigma/k_BT$. This implies that the activation energy needed for transport increases upon lowering the temperature. When raising the Fermi level to $E_F = 3\sigma$, i.e., close to the equilibrium energy, the dependence of $qD/\mu k_BT$ on σ/k_BT becomes weaker. Consistent with earlier work [8–10], the calculations show that $qD/\mu k_BT$ increases quadratically with electric field and the effect increases when going from a 1D to a 3D system (Fig. 2). This is a signature of anomalous spreading of the carrier packet in a disordered system in the presence of a bias field. Physically, mobility reflects carrier motion down-field while diffusion reflects three-dimensional motion. The Einstein relation applies when motion in all three directions is equivalent, which is only at low field. The Einstein relation does not apply under high-field conditions when the down-field motion is very different in magnitude compared to motion in the perpendicular directions.

Next, we examine in greater detail how $qD/\mu k_BT$ changes upon filling up the DOS distribution by raising the Fermi level in Fig. 3. This anomalous spreading of the carrier packet is caused by filling the DOS as evidenced by the variation of the carrier mobility, their diffusivity and $qD/\mu k_BT$ as a function of the concentration of the charge carriers. The carrier concentration is calculated from Eq. (3). Figure 3 shows also data for $\sigma/k_BT = 2.3$ in which the quasiequilibrium energy,

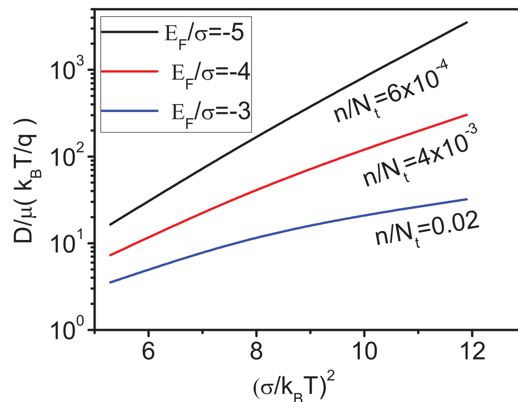

FIG. 1. (Color) Dependence of $qD/\mu k_BT$ as a function of the disorder parametric in the normalized Fermi level E_F/σ (carrier concentration).

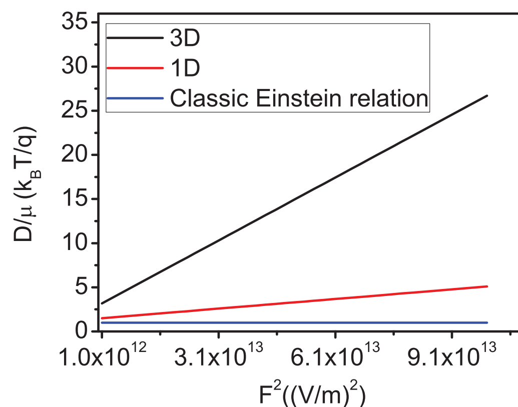

FIG. 2. (Color) Dependence of $qD/\mu k_BT$ on the electric field. The parameters are $\sigma = 0.06$ eV and $E_F = -0.35$ eV. The other parameters are the same as those in Fig. 1

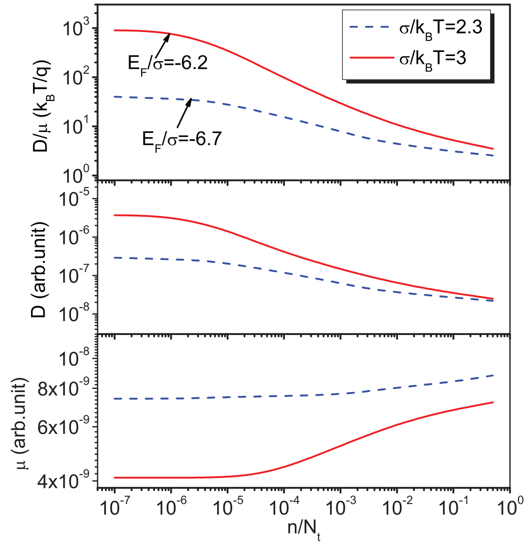

FIG. 3. (Color) (Top) Dependence of the charge carrier mobility μ (bottom), the diffusivity D (middle) and $qD/\mu k_B T$ (top) as a function of the relative charge carrier concentration for a 3D system and $F = 1 \times 10^7$ V/m. The arrows indicate the relative positions of the Fermi level at which the $qD/\mu k_B T$ begins to fall off.

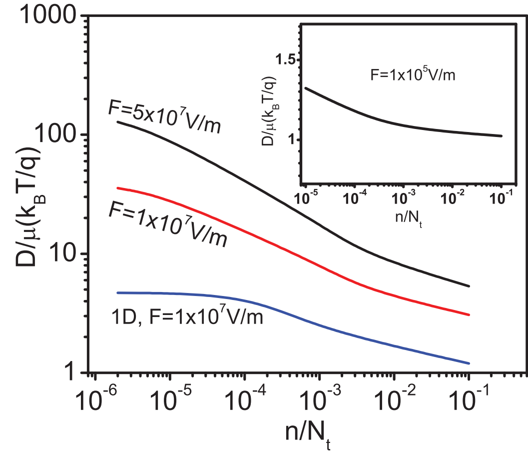

FIG. 4. (Color) Dependence of $qD/\mu k_B T$ on carrier concentration for different electric fields for 3D system and for $F = 1 \times 10^7$ V/m for a 1D system. The disorder parameter $\sigma/k_B T$ is $\sigma/k_B T = 2.3$. The inset shows the dependence of $qD/\mu k_B T$ for 3D on the carrier concentration at low electric fields.

normalized to σ, is at $-\sigma/k_B T = -2.3$. At low lying Fermi level, i.e., when the DOS is virtually empty, the charge carrier mobility is independent on carrier concentration and starts increasing weakly around $n/N_t = 1 \times 10^{-4}$, consistent with earlier work [26,27]. Remarkably, the field-assisted diffusivity begins to decrease already at a relative concentration of the order of $n/N_t = 1 \times 10^{-6}$, equivalent to a normalized Fermi level at E_F/σ of 6.7 ($\sigma/k_B T = 2.3$) and 6.2 ($\sigma/k_B T = 3$). The $qD/\mu k_B T$ ratio decreases accordingly. Nenashev *et al.* [9] argued already that the deep are responsible for the anomalous spreading of the carrier packet. This is, by the way, difficult to assess via Monte Carlo simulation because of the requires huge site array but is easily taken care of in the current analytic calculations.

The notion that the decrease of both D and $qD/\mu k_B T$ is associated with the deep tail states of the DOS is plausible because deeply localized trapped carriers are more strongly localized and lag behind the packet of moving carriers. Eliminating those deep states by raising the Fermi level must therefore reduce field assisted diffusion as illustrated in Fig. 3(middle). The effect of deep states is also diminished by raising the temperature. This is documented by the facts that(i) the diffusivity decreases exponentially with $(\sigma/k_B T)^2$ whereas the mobility increases with $(\sigma/k_B T)^2$ and (ii) that the slope of $ln(qD/\mu k_B T)$ versus $(\sigma/k_B T)^2$ decreases upon raising the Fermi level.

Figure 4 shows that the decrease of $qD/\mu k_B T$ with increasing n/N_t diminishes upon lowering the electric field because the anomalous spreading of the carrier is a field-driven process. It is clear here, at high electric field, $qD/\mu k_B T$ decreases with carrier density, which is contradictory to the prediction of Eq. (2). The inset in Fig. 4 demonstrates that at low electric field (1×10^5 V/m), $qD/\mu k_B T$ indeed approaches unity when the concentration reaches about $n/N_t = 1 \times 10^{-3}$. Interestingly, though, $qD/\mu k_B T$ tends to level off at high carrier concentration and higher fields suggesting that in this case, the Einstein relation is violated, probably because of charge carrier heating. The observation that $qD/\mu k_B T = 1$ is recovered at low fields is consistent with the simulations of Mendels and Tessler for a field of $F = 5$ V/m [14].

In summary, we show that, at low fields, the Einstein relation applies correctly to organic semiconductors, however, at a higher electric field regime, the Einstein relation deviates dramatically, this should be expected in any material including organic semiconductors. We have also shown that anomalous field assisted diffusion is a fictitious phenomenon, caused by the spatial displacement between a moving charge carrier front and strong localized carriers that lag behind as electric field and disorder increase. This effect is gradually diminished when either those deep states are filled by raising the Fermi level or by increasing temperature when the occupational DOS shifts towards the center of the DOS. The interplay between the operationally defined diffusion and drift of charge carriers, expressed by the Einstein ratio, is a temperature and field driven process. It is gradually eliminated upon filling up the states in a hopping system with the Gaussian DOS distribution.

We would also point out that the MA model is actually a good approximation for Marcus theory in equilibrium mode [16], the choice of the hopping rate only affects the temperature dependence of the averaged jump rate because an extra term for the geometric relaxation energy enters, this term is unimportant for charge carrier hopping near room temperature. The Marcus rate equation can be also included in our model (see Appendix B).

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APPENDIX A

The hopping probability between two sits depends on their spatial separation and energy difference, described as Miller equation (4). The transport of the carrier through a semiconductor layer consists of a series of hops, therefore, the net conductivity depends on the average of the probabilities of sequential hops. As sequential probabilities multiply, the appropriate average is the geometric mean, i.e., $\langle P\rangle = \lim_{\Lambda\to\infty}[\prod_i^{\Lambda} P_i]^{1/\Lambda} = \exp(\lim_{\Lambda\to\infty}\frac{1}{\Lambda}\sum_i^{\Lambda}\ln P_i)$ [17,20], where P_i is the probability of the individual hop. Defining $P_i = \exp(-R)$ results in $\langle P\rangle \sim \exp(-\langle R\rangle) = \exp(-R_{nn})$, and R_{nn} is the average range hopped by a particular carrier on its passage through the material. For an quasiequilibrium system, this value should be the same for this particular carrier.

APPENDIX B

In the case of the Marcus jump rate model, the probability of carrier jump from a site with energy normalized ϵ_i to the target site with energy ϵ_j is given [28,29]

$$\nu = \frac{|I_{ij}|^2}{\hbar k_B T}\sqrt{\frac{\pi}{\epsilon_a}}\exp\left[-\frac{(\epsilon_j-\epsilon_i+\epsilon_a)^2}{4\epsilon_a}\right]. \quad \text{(B1)}$$

Here, $\epsilon_d = E_a/k_BT$ with E_a being the reorganisation energy related to the polaron relaxation, $I_{ij} = J_0\exp(-2\alpha R_{ij})$ is the transfer integral, i.e., the wave-function overlap between sites i and j. Similar to Eq. (4), when electric field F exists, Marcus hopping rate can be written as

$$\nu = \frac{|I_{ij}|^2}{\hbar k_B T}\sqrt{\frac{\pi}{\epsilon_a}}\exp\left[-\frac{\left(\epsilon_j-\epsilon_i+\frac{qFR_{ij}\cos\theta}{k_BT}+\epsilon_a\right)^2}{4\epsilon_a}\right]$$
$$= \nu_0\exp\left[-2r_{ij}-\frac{\left(\epsilon_j-\epsilon_i+\frac{qFR_{ij}\cos\theta}{k_BT}+\epsilon_a\right)^2}{4\epsilon_a}\right].$$

In this situation, the hopping range can be presented as

$$R = 2r_{ij} + \frac{(\epsilon_j-\epsilon_i+\beta r_{ij}\cos\theta+\epsilon_a)^2}{4\epsilon_a}. \quad \text{(B2)}$$

Then, according to the definition of the average hopping range in the manuscript, R_{nn} can be obtained by solving

$$B_c = \frac{1}{8\alpha^3}\int_0^{\pi} d\theta\sin\theta\int_0^{R_{nn}/2} dr 2\pi r^2 \times\int_{\epsilon_i-\epsilon_a-\beta\cos\theta r-\sqrt{4\epsilon_a(R_{nn}-2r)}}^{\epsilon_i-\epsilon_a-\beta\cos\theta r+\sqrt{4\epsilon_a(R_{nn}-2r)}} d\epsilon\tau(\epsilon,\epsilon_F).$$

Again, following the definition of $\bar{x}_f$ in the manuscript, one can obtain

$$\bar{x}_f = \frac{I_1}{I_3} \quad \text{(B3)}$$

with

$$I_1 = \int_0^{\pi} d\theta\sin\theta\int_{\epsilon_i-\epsilon_a-\text{Max}((4\epsilon_aR_{nn})^{1/2},0.5\beta R_{nn}\cos\theta)}^{\epsilon_i-\epsilon_a+(4\epsilon_aR_{nn})^{1/2}} d\epsilon\tau(\epsilon,\epsilon_F) \times\left(\frac{-B\pm\sqrt{B^2-4AC}}{2A}\right)^3\cos\theta.$$

$$I_3 = \int_0^{\pi} d\theta\sin\theta\int_{\epsilon_i-\epsilon_a-\text{Max}((4\epsilon_aR_{nn})^{1/2},0.5\beta R_{nn}\cos\theta)}^{\epsilon_i-\epsilon_a+(4\epsilon_aR_{nn})^{1/2}} d\epsilon\tau(\epsilon,\epsilon_F) \times\left(\frac{-B\pm\sqrt{B^2-4AC}}{2A}\right)^2,$$

where

$$A = \beta^2\cos^2\theta,\quad B = 2\beta\cos\theta(\epsilon-\epsilon_i+\epsilon_a)+4\epsilon_a$$
$$C = (\epsilon-\epsilon_i+\epsilon_a)^2 - 4\epsilon_aR_{nn}.$$

Then

$$t(\epsilon) = \frac{I_1'}{I_2'}, \quad \text{(B4)}$$

$$I_1' = \int_0^{\pi} d\theta\sin\theta\int_0^{R_{nn}/2} dr 2\pi r^2\int_{\epsilon_i-\epsilon_a-\beta\cos\theta r-\sqrt{4\epsilon_a(R_{nn}-2r)}}^{\epsilon_i-\epsilon_a-\beta\cos\theta r+\sqrt{4\epsilon_a(R_{nn}-2r)}} \times d\epsilon\tau(\epsilon,\epsilon_F)\frac{\exp\left[4\alpha+\frac{\left(\epsilon_j-\epsilon_i+\frac{qFR_{ij}\cos\theta}{k_BT}+\epsilon_a\right)^2}{4\epsilon_a}\right]}{\nu_0},$$

$$I_2' = \int_0^{\pi} d\theta\sin\theta\int_0^{R_{nn}/2} dr 2\pi r^2\int_{\epsilon_i-\epsilon_a-\beta\cos\theta r-\sqrt{4\epsilon_a(R_{nn}-2r)}}^{\epsilon_i-\epsilon_a-\beta\cos\theta r+\sqrt{4\epsilon_a(R_{nn}-2r)}} \times d\epsilon\tau(\epsilon,\epsilon_F).$$

Substituting Eqs. (14) and (15) into (6), (9), and (10), D/μ based on Marcus rate can be calculated. It can be seen from Fig. 5, though the dependence of D/μ is not so strong as Miller equation, the basic trend is the same. This conclusion holds for the field and temperature dependence of D/μ as well.

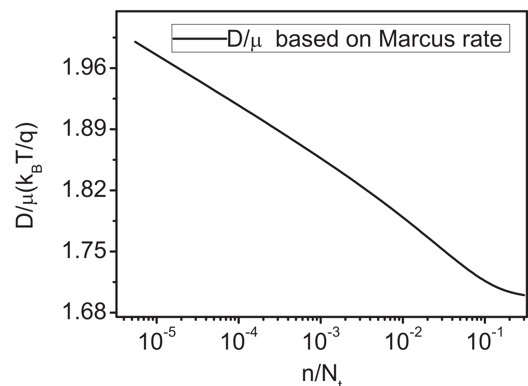

FIG. 5. Dependence of D/μ on carrier density. The parameters used here are $F = 1\times10^7$ V/m, $\sigma/k_BT = 3$ and $E_a = 0.5$ eV. The other parameters are the same as those in Fig. 1.

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