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Universal carrier thermoelectric-transport model based on percolation theory in organic semiconductors

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Recent measurements conducted over a large range of temperature and carrier density have found that the Seebeck coefficient exhibits an approaching disorder-free transport feature in high-mobility conjugated polymers [D. Venkateshvaran *et al.*, Nature **515**, 384 (2014)]. It is difficult for the current Seebeck coefficient model to interpret the feature of the charge transport approaching disorder-free transport. We present a general analytical model to describe the Seebeck effect for organic semiconductors based on the hopping transport and percolation theory. The proposed model can well explain the Seebeck feature of the polymers with approaching disorder-free transport, as well as that of the organic semiconductors with the general disorder. The simulated results imply that the Seebeck coefficient in the organic semiconductors would happen to transfer from temperature dependence to temperature independence with the decrease of the energetic disorder.

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I. INTRODUCTION

The charge transport mechanism is among the most often discussed topics in the field of disordered systems, particularly organic semiconductors. The central question is how carriers transport themselves between spatially localized states. To clearly understand the intrinsic nature of charge transport in organic semiconductors, numerous researchers have performed theoretical and experimental studies and concluded that the charge carrier transport is generally characterized by hopping between localized states of Gaussian or exponential distribution of the density of states (DOS) [1–5]. For a long time, one prevalent parameter of the charge transport in organic semiconductors is the charge carrier mobility, which provides a quantitative estimate for the performance of organic semiconductor devices. A pioneering hopping transport model describing the charge carrier mobility is the Gaussian disorder model (GDM) suggested by Bässler [6]. Following the GDM, numerous theoretical models in disordered organic semiconductors have been established to further investigate the charge transport property [7–9]. However, due to the use of a large number of free parameters, the validity and accuracy of the charge carrier mobility from these current models has been questioned, in spite of good agreement between the simulated results and experimental data [10]. On the other hand, with the decrease of the device size accompanying the channel length in transistors, the contact effect in the interface plays a great role in the charge transport characteristics [11,12].

In order to overcome these deficiencies in the current transport models, other key transport parameters, such as the Seebeck coefficient, should be applied to promote a more credible and accurate transport process in organic semiconductor devices. It is well known that the Seebeck coefficient not only governs the efficiency of thermoelectric converters, but also provides unique, complementary insight into the electronic structure of functional material [13]. More importantly, the Seebeck voltage is independent of the interfacial contact [14]. Hence the Seebeck coefficient can veritably reveal the intrinsic characteristics of the charge carrier transport. In the past decade, several models of Seebeck coefficient have been proposed in organic semiconductors, based on the general Seebeck coefficient expression [15–17], $s = \frac{\int (E-E_f)G(E)dE}{qT\int G(E)dE}$, which is determined by the difference between Fermi level E_f and the energy E. Here $G(E)$ is the conductivity distribution function, T is the temperature, and q is the charge of the carrier. However, recent measurements conducted over a large range of temperature and carrier density have found that in high-mobility conjugated polymers the Seebeck coefficient exhibits an approaching disorder-free transport (disorder-free transport is defined as the energetic disorder relative to $k_{\mathrm{B}}T$ associated with transport) [18], at which the measurement of the Seebeck coefficient was performed in field-effect transistors (FETs). It is difficult for the current Seebeck coefficient expression to describe the feature of the charge transport approaching disorder-free transport. In addition, the authors attempted to interpret this phenomenon in terms of the variable-range hopping disorder model used in Ref. [19], but it broke down for indacenodithiophene-co-benzothiadiazole (IDTBT). On the other hand, the authors suggested a simpler, more consistent interpretation of the three salient Seebeck features given by a narrow-band model, which is applicable to all polymers [18]. However, the simulated results calculated by the narrow-band model exhibit a low estimation of the Seebeck coefficient, especially for poly(2,5-bis(3-alkylthiophen-2-yl)thieno(3,2-b) thiophene) (PBTTT) and selenophene-based polymer semiconductor (PSeDPPBT).

In this work, we present a general analytical model to describe the Seebeck effect for organic semiconductors based on the hopping transport and percolation theory. The proposed model can well interpret the Seebeck feature of the polymers with approaching disorder-free transport, as well as that of the organic semiconductors with the general disorder.

II. THEORY MODEL

Our starting point is the following general definition for Seebeck coefficient S. In semiconductors, charges carry heat from one place to another. The heat Q carried by the charges

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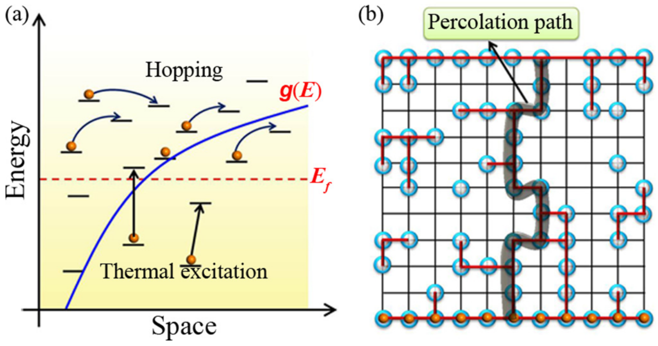

FIG. 1. (Color online) (a) Schematic diagram of carrier transport in hopping space with the density of states, and (b) the corresponding percolation current in disordered organic semiconductor.

contributing to the electrical current I is given as $Q = I \times \Pi$, where Π is the Peltier coefficient which represents how much heat is carried per unit charge. The Seebeck coefficient is then related through the Kelvin-Onsager relation to the Peltier coefficient as [20,21]

$$S = \frac{\Pi}{T}. \tag{1}$$

The charge transport in disordered organic semiconductors can be widely described by hopping and percolation theories. Under a percolation model, a random-resistor network connecting each molecular site is often used in the hopping system. Figure 1 shows the schematic diagram of the charge transport in a hopping system and the corresponding percolation current through the polymer matrix for the carrier to travel through.

A percolation theory to calculate Peltier coefficient Π based on hopping transport has been developed in the literature [22,23]. In this theory, Π is identified with the average site energy on percolation cluster and can be written as

$$\Pi = \int E_i P(E_i)\, dE_i, \tag{2}$$

where $P(E_i)$ is the probability that a site of energy E_i is on the current-carrying percolation cluster and was further given by

$$P(E_i) = \frac{g(E_i) P_1(Z_m|E_i)}{\int_{-E_m}^{E_m} g(E_i) P_1(Z_m|E_i) dE_i}, \tag{3}$$

where $g(E_i)$ is the density of states per unit volume, E_m is the maximum site energy, and $P_1(Z_m|E_i)$ is the probability that the second smallest resistance emanating from a site with energy E_i is not larger than the maximum resistance on the percolation cluster, Z_m. The expression of the probability $P_1(Z_m|E_i)$ is written as

$$P_1(Z_m|E_i) = 1 - \exp[-P(Z_m|E_i)][1 + P(Z_m|E_i)], \tag{4}$$

where $P(Z_m|E_i)$ is the bond density, which means the average value of resistance of Z_m or less connected to a site energy E_i. To calculate the Peltier coefficient (or Seebeck coefficient), an expression for $P(Z_m|E_i)$ is essential.

According to the percolation theory, the disordered organic semiconductor system is viewed as a random-resistor network [see Fig. 1(b)]. To determine the total conductivity in a disordered system, the first step is to take a reference conductance H and remove all conductive pathways between sites i and j with $H_{ij} < H$. The conductance between sites i and j is given by $H_{ij} \propto \exp(-S_{ij})$ with [24]

$$S_{ij} = 2\alpha R_{ij} + \frac{|E_i - E_f| + |E_j - E_f| + |E_i - E_j|}{2k_B T}, \tag{5}$$

where R_{ij} is the hopping distance, α is the inverse localized length, and E_f is the Fermi level.

The density of bonds $P(Z_m|E_i)$ then can be written as

$$P(Z_m|E_i) = \int 4\pi R_{ij}^2 g(E_i) g(E_j) dR_{ij} dE_i dE_j \theta(S_c - S_{ij}). \tag{6}$$

If the density of participating sites is P_s, the critical parameter S_c is found by solving the equation

$$P(Z_m|E_i) = B_c P_s = B_c \int g(E) dE \theta(S_c k_B T - |E - E_f|). \tag{7}$$

Based on the numerical studies for a three-dimensional amorphous system, the formation of an infinite cluster corresponds to $B_c = 2.8$ [24–26].

By connecting Eqs. (5)–(7), the bond density can be formulated as

$$P(Z_m|E_i) = \frac{4\pi}{3(2\alpha)^3} \left\{ \begin{array}{l} \int_{\epsilon_f}^{\epsilon_i} (S_c - \epsilon_j + \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_i}^{S_c + \epsilon_f} (S_c - \epsilon_j + \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_i - S_c}^{\epsilon_f} (S_c - \epsilon_i + \epsilon_j)^3 g(\epsilon_j) d\epsilon_j,\ \epsilon_i > \epsilon_f \\ \int_{\epsilon_i}^{\epsilon_f} (S_c + \epsilon_i - \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_f - S_c}^{\epsilon_i} (S_c + \epsilon_i - \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_f}^{\epsilon_i + S_c} (S_c - \epsilon_j + \epsilon_i)^3 g(\epsilon_j) d\epsilon_j,\ \epsilon_i < \epsilon_f \end{array} \right\}. \tag{8}$$

Here ϵ is the normalized energy as $\epsilon = \frac{E}{k_B T}$. This expression has been split into two regimes of $\epsilon_i > \epsilon_f$ and $\epsilon_i < \epsilon_f$, which are corresponding to the contributions of ϵ_i above or below the Fermi level to $P(Z_m|E_i)$ and therefore the Seebeck coefficient S, respectively. Above the Fermi level, carriers in shallow states will move by hopping to other shallow states. While below the Fermi level, carriers in deep states will move by thermal excitation to shallower states.

Now we can substitute Eqs. (2)–(4) and (8) into Eq. (1) and obtain the final result of the Seebeck coefficient.

As mentioned above, because the experimental results of the Seebeck coefficient from Ref. [18] were measured by using FETs, we now proceed to calculate the Seebeck coefficient in organic FETs by introducing the carrier density specifically. In bulk material, the carrier density n is related to the density of states and the Fermi-Dirac distribution function in the form

$$n = \int \frac{g(E)}{1 + \exp\left(\frac{E-E_f}{k_B T}\right)} dE, \tag{9}$$

where $g(E)$ is the density of states which is assumed to be the Gaussian distribution in this work, $g(E) = \frac{N_t}{\sqrt{2\pi}\sigma_0}\exp(-\frac{E^2}{2\sigma_0^2})$; N_t is the number of states per unit volume; and $\sigma_0 = \sigma/k_B T$ indicates the width of the density of states (DOS).

In a FET, however, the distribution of carrier density is not uniform, which decreases with the distance from the semiconductor-insulator interface. In this situation, the carrier density corresponding to the Fermi level is controlled by gate voltage V_g through Gauss's Law as [27]

$$V_g - V_{\rm th} - \varphi_s = \frac{1}{C_i}\sqrt{2q\varepsilon_s \int_0^{\varphi_s} \int_{-\infty}^{\infty} \frac{g(E)}{1 + \exp[(E - E_f)/k_B T]} dE d\varphi}, \tag{10}$$

where $E_f = E_{f0} + q\varphi$ with E_{f0} denoting the Fermi level as $V_g = 0$, V_{th} is the threshold voltage defined as the gate bias at the onset of accumulation, ε_s is the dielectric constant of the semiconductor, and φ_s is the surface potential. By combining Eqs. (1) and (9) with (10), we can obtain the gate voltage–dependent Seebeck coefficient.

III. RESULTS AND DISCUSSION

Firstly, we compare the simulation results with the experimental data of the Seebeck coefficient measured by using FET from three kinds of conjugated polymers, i.e., IDTBT, PBTTT, and PSeDPPBT [18]. Figure 2 shows the carrier density dependence of the Seebeck coefficient with the comparison between the calculation and experimental data for different conjugated polymers. One can see that the proposed model can reasonably reproduce the experimental data under the whole range of carrier density for the polymers with a disorder-free or a large energetic disorder. Here we use the same density of thermally accessible sites as those in Ref. [18], i.e., $N_t = 7.4 \times 10^{20}\,\mathrm{cm}^3$ (IDTBT), $N_t = 8.9 \times 10^{20}\,\mathrm{cm}^3$ (PBTTT), and $N_t = 2 \times 10^{20}\,\mathrm{cm}^3$ (PSeDPPBT). Other fitting parameters are the typical value for the conjugated polymers, for example, $\varepsilon_s = 3$, $\epsilon_{f0} = -40\ k_B T$, $C_i = 1 \times 10^{-4}\ \mathrm{F/m}^2, \alpha^{-1} = 0.1\,\mathrm{nm}$ (for IDTBT and PBTTT), and $\alpha^{-1} = 0.22\,\mathrm{nm}$ (for PSeDPPBT). Otherwise, the energetic disorder $\sigma = 1.2$, 3.5, and $5\,k_\mathrm{B}T$ are used for IDTBT, PBTTT, and PSeDPPBT, respectively. Please note that the energetic disorder of $\sigma = 1.2\,k_\mathrm{B}T$ for IDTBT approaches disorder free. According to the result of Ref. [18], IDTBT is disorder free, and the energetic disorder is significantly lower in IDTBT than that in PBTTT and PSeDPPBT. Thus our results are well consistent with that of the literature [18].

Carrier density dependence of the Seebeck coefficient for the different temperatures is plotted for PBTTT and IDTBT in Fig. 3. The input parameters are the same as those in Fig. 2. It is found that the Seebeck coefficient shows the same decreasing trend with temperature for IDTBT, which implies it is the temperature independent, whereas the Seebeck coefficient shows the variable decreasing trend with temperature for PBTTT; that is, at low temperature the carrier density dependence is stronger than that at higher temperature. As mentioned above, the energetic disorder in IDTBT is significantly lower than that in PBTTT. Therefore, the temperature-independent feature of the Seebeck coefficient should be induced by the smaller energetic disorder. The simulation results agree well with the experimental data for IDTBT and PBTTT.

Many researchers have reported that the Seebeck coefficient has the temperature-independent property for the organic semiconductors with disorder free (IDTBT) or single crystals (pentacene and rubrene) [15,18]. To better understand the temperature-independent feature of the Seebeck coefficient, we then discuss the effect of energetic disorder and temperature on the Seebeck coefficient. Figure 4(a) shows the energetic disorder dependence of the Seebeck coefficient at 200 and 300 K. One can see that the Seebeck coefficient shows

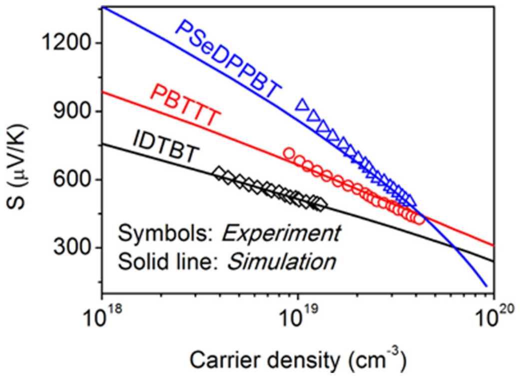

FIG. 2. (Color online) Carrier density dependence of Seebeck coefficient for different materials at room temperature. Symbols and solid lines are experimental and simulated results, respectively.

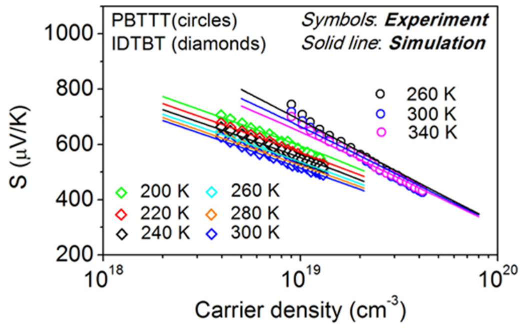

FIG. 3. (Color online) Temperature dependence of Seebeck coefficient for PBTTT and IDTBT. Symbols and solid lines are experimental and simulated results, respectively.

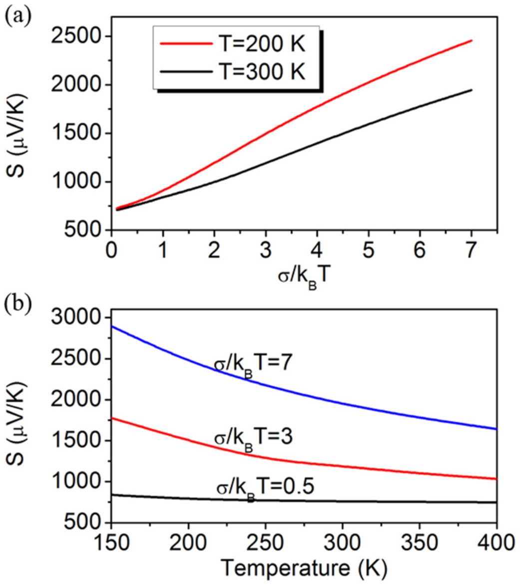

FIG. 4. (Color online) (a) Energetic disorder dependence of Seebeck coefficient at 200 and 300 K, and (b) temperature dependence of Seebeck coefficient for different energetic disorder.

strong energetic disorder dependence. This dependence under the larger energetic disorder will enhance with decreasing the temperature. For the smaller energetic disorder, such as $\sigma/k_B T < 1$, this dependence is similar for different temperatures. Temperature dependence of the Seebeck coefficient for different energetic disorders is plotted in Fig. 4(b). The observed results clearly show that the temperature dependence enhances with increasing energetic disorder.

Generally, carriers in deep states will move by thermal excitation to shallower states, while carriers in shallow states will move by hopping to other shallow states. If the carrier is initially generated randomly within the DOS, it tends to relax towards tail states; the typical rate at which carriers hop away from a state is much smaller for deeper initial energy. Otherwise, the Seebeck coefficient is dominated by the entropy of mixing associated with adding a carrier into the density of states, which is determined by the density of thermally accessible transport states [18,28,29]. Therefore, for the smaller energetic disorder, the density of thermally accessible transport states will remarkably decrease. As a result, the Seebeck coefficient shows the temperature independence. Figure 5 clearly shows the contribution to the Seebeck coefficient of carriers above the Fermi level (shallow state) and below the Fermi level (deeper state), respectively. Here $S_{(E<E_f)}$ and $S_{(E>E_f)}$ denote the contributions of carriers below or above the Fermi level, respectively. The overall Seebeck coefficient is calculated as $S = S_{(E>E_f)} - S_{(E<E_f)}$. One can see that the Seebeck coefficient from the contribution of carriers below the Fermi level reduces remarkably with the decrease of the energetic disorder. Thus the Seebeck coefficient is attributed to the carriers in shallow states by hopping to other shallow states and will imply the temperature independence for the smaller energetic disorder.

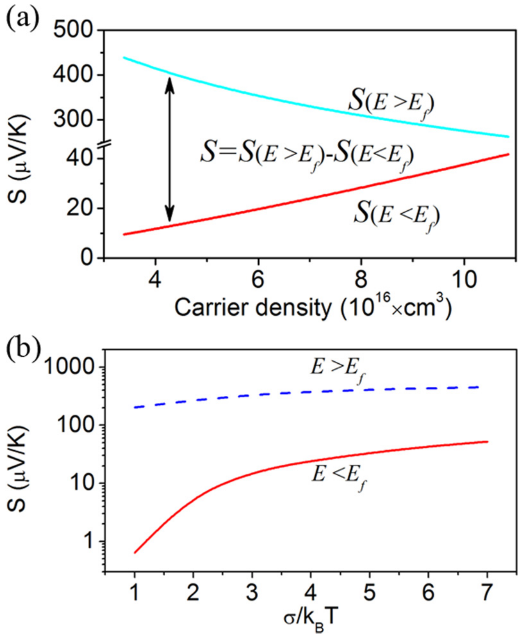

FIG. 5. (Color online) Contribution to the overall Seebeck coefficient of carriers below $S_{(E<E_f)}$ or above $S_{(E>E_f)}$ Fermi level as a function of carrier density at $\sigma/k_B T = 3.5$ (a) and energetic disorder (b). The input parameters are $N_t = 5 \times 10^{20}\,\mathrm{cm}^3$, $\alpha^{-1} = 0.15\,\mathrm{nm}$, $T = 300\,\mathrm{K}$. The other parameters are the same as those in Fig. 2.

IV. CONCLUSION

A general analytical model is proposed to describe the Seebeck effect for organic semiconductors based on the hopping transport and percolation theory. The proposed model can well interpret the Seebeck feature of the polymer with approaching disorder-free transport, as well as that of the organic semiconductors with the general disorder. The simulation results display that the feature of the Seebeck coefficient would transfer from temperature dependence to temperature independence, which is induced by the smaller energetic disorder. The simulation results agree well with the experimental data for IDTBT and PBTTT.

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