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Dependence of general Einstein relation on density of state for organic semiconductors

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ABSTRACT

The Einstein relation (ER) about the diffusion coefficient D and mobility μ of charge carriers has been suspected for disordered organic semiconductors. The general Einstein relation (GER) is popular in recent years, and usually been calculated based on the Gaussian DOS. A clearly cutting inverse-exponential (CCIE) DOS [Org. Elect. 30 (2016) 60–66] is proposed. The mobility is obtained by solving variable range hopping (VRH) equations. The results show that the experimental mobility-density data can be well fitted by using single CCIE DOS in the wide ranges of density, but cannot be fitted by using single Gaussian or un-cutting exponential-type DOS. In this work, the coefficient ζ in the GER ($D/\mu = \zeta kT/q$) is calculated based on the Gaussian and CCIE DOSs. The variations of coefficient ζ with temperature and density are analyzed. It is shown that the ζ are a gradually decreasing function with temperature and similar for both DOSs. But variations of ζ with density are very different for both DOSs. The ζ is a gradually increasing function of density for the Gaussian DOS, but a non-monotonously increasing function of density for the CCIE DOS with a platform located in the typical range of density. The ζ is assumed as a constant to analyze the data of ideality factor for two organic diodes based on rr-P3HT and OC_1C_{10}-PPV in literature, the theoretical results are in agreement with experimental data.

1. Introduction

Organic semiconductors are focus of attention for many relevant disciplines because of applications such as organic light-emitting diodes (OLED) [1,2], field-effect transistors (OFET) [3,4], photovoltaic devices [5–7], and sensors [8,9], and merits such as their low-cost, low weight, mechanical flexibility and large-area, etc. Charge-carrier transport is a fundamental issue of disordered organic semiconductors. Although the charge transport mechanism is recognized as controlled by hopping between different sites, many aspects have not been clarified at present [10–12]. Experiments and simulations [11–25] have shown that the transport mechanism deviates significantly from the inorganic semiconductors, and some works proposed the ratio between the diffusion coefficient D and the mobility μ of charge carriers is larger than the Einstein relation (ER) of $D/\mu = kT/q$ [11]. Here k is the Boltzmann constant, T is the temperature, and q is the elementary charge. The ratio D/μ is a key factor not only to determine transport properties, but also to be an implication of degeneracy of charge carriers.

The generalized Einstein relation (GER) has been firstly derived for high-density (degenerate) crystalline semiconductors [12] or amorphous semiconductors having a band tail [13–16]. Richert et al. [14,15] made Monte Carlo (MC) simulations based on a Gaussian distribution of sites, their results show that the ratio D/μ significantly deviates from Einstein's kT/q. Baranovskii et al. [16] measured photoconductivity in amorphous semiconductors being determined by the energy-loss hopping of carriers through localized band-tail states, their analysis shows that the data cannot be explained by using the model based on the ER. Hirao et al. [17] proposed that the ER cannot be held for molecularly doped polymers (MDP), and both the D and μ of the MDP need to be measured separately.

Roichman and Tessler [18] firstly proposed the GER for organic semiconductors, they calculated the ratio D/μ for organic semiconductors based on the Gaussian density of states (DOS) and the assumption that the system is close to quasi-equilibrium. Their numerical results of D/μ are in good agreement with the values deduced from MC simulations of Richert et al. [15]. They [18] analyzed the impact of GER to performance of devices, and

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showed the effect of GER plays an important role for the contact phenomena and exciton generation rate existing in OLEDs and OFETs. They [19] also compared the GER deduced from Gaussian and exponential DOSs, they find that the shape of the DOS affects the ideality factor of p–n diodes. Tessler also [20] pointed out that the radio D/μ significantly deviate from ER under nonequilibrium conditions. He advised to use the ER when the charge density is low enough, and adopt the GER when the charge density is high.

Peng et al. [21–23] calculated the ratio D/μ for doped organic semiconductors based on the Gaussian DOS for the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The numerical results show that, the ER holds for low carrier concentrations, but changes strongly with the electron (hole) concentration, the doping level, the mean energy of LUMOs (HOMOs) of the dopant and the host, as well as their variances [21–23]. Lu et al. [24] extended the GER to consider the potential energy of carriers in an electric field (PDGER). The electric-field dependence of GER can be equivalently seen as having position-dependent Fermi energy, and implies the organic semiconductor is in non-equilibrium under an electric field.

Richert et al. [15] calculated the radio of D/μ as a function of the width of DOS σ and electric field F based on the Gaussian DOS by employing the Monte Carlo simulations. Their results show that the ER is violated when the system is not at steady state. Mendels and Tessler [25] also made Monte Carlo simulations to check applicability of GER. They showed that the GER is sufficiently accurate for practical use at low fields, and proposed an energy flux model to provide a more transparent and intelligible description instead of the GER. Li et al. [26] calculated the GER based on the Gaussian DOS as a function of disorder, temperature, bias field, and Fermi level, i.e., concentration of occupied states of the DOS under the condition of quasi-equilibrium. They showed that, at low fields, the ER applies correctly to organic semiconductors, however, at a higher electric field regime, the ER deviates dramatically, and this should be expected in any material including organic and inorganic semiconductors.

Leary and Johnson [27] have ever proposed a combining DOS with exponential distributions of tail states and square-root distributions of band states. Nguyen and Leary [28] applied the DOS to calculate the ratio D/μ of GER. Recently, Çopuroğlu and Mehmetoğlu [29] derived a semi-analytic expression of GER based on the binomial expansion theorems and the combining DOS. Considering that the combining DOS is not popular as compared with Gaussian DOS, and our recently work [30] don't support the exponential tail, so we don't consider the combining DOS in this work.

Koster et al. [31], Harada et al. [32] and Epstein et al. [33] measured a temperature dependent ideality factors for organic solar cells, the data is in inverse proportion to temperature, and is in accordance with prediction by the GER [18]. Although many works support the GER for organic semiconductors [14–33], Wetzelaer et al. [34] pointed out that it is controversial whether energetic disorder in semiconductors is already sufficient to violate the ER, even in the case of thermal equilibrium. They [34] demonstrated that the ER is violated only under nonequilibrium conditions due to deeply trapped carriers, and proved the validity of the ER in disordered semiconductors in thermal (quasi)equilibrium. Their demonstration [34] is based on the ideality factor for OLEDs extracted by using the Shockley diode equation to fitting current-voltage data. Based on the conclusion of Wetzelaer et al. [34], the ER has been widely used in modeling OLEDs and OFETs [2–4,6–10].

Except for the GER, the form of DOS also is a key problem of organic semiconductors. The Gaussian DOS is the most popular in researches of organic semiconductors

$$G(E) = \left(N_0 \Big/ \sigma\sqrt{2\pi}\right)\exp\left[-(E-E_v)^2 \Big/ 2\sigma^2\right] \tag{1}$$

σ is the width, N_0 is the total concentration of states at energy levels E_v. The exponential DOS is also widely used for analytic formulae being accessible in some models

$$G(E) = (N_0/\sigma)\exp[(E-E_v)/\sigma],\ (-\infty < E \le E_v) \tag{2}$$

Torricelli et al. [35] proposed the DOS for different materials can be a single Gaussian, an exponential, or by a combination of both functions. Oelerich et al. [36] proposed following general DOS with λ as the adjustable parameter through qualitatively comparing their expression with experimental data, they [36] concluded that λ should take values larger than 1.8, and the DOS is more likely the Gaussian form. Welborn et al. [37] used free probability to approximate the DOS in tight-binding models of disordered electronic systems, they found that the DOS can take both Gaussian and non-Gaussian forms for different parameter values. Tessler et al. [38] studied the *I-V* characteristics of *p-n* diodes based on three types of DOS (exponential, Gaussian, and Gaussian with exponential tail) to analyze the dependence of GER to the form of DOS. The results show that the form of DOS would greatly influence the GER factor and the GER factor is an increasing function of the width of DOS.

$$G(E) = (N_0/\sigma)\exp\left[-(E_v-E)^{\lambda} \Big/ \sigma^{\lambda}\right],\ (-\infty < E \le E_v) \tag{3}$$

Based on above statement, it can be seen that the system is not at steady state [15,23,26,34] or the type and the width of DOS [19,38] or the charge density [20–24] can results in the deviation from the ER. In this work we mainly discuss the influence of the shape of DOS with the GER. Although many works [18–26] about the GER are based on the Gaussian DOS, but some works are based on exponential DOS [19] or combining DOS [21–23]. In one of our recent work [30], we proposed three exponential-type **DOSs**, one has complete exponential tail, and other two cuts tails at some places. The variations of mobility with carrier density are obtained through numerically solving variable range hopping (VRH) equations. The results show that the experimental mobility-density data can be well fitted by using single clearly cutting inverse-exponential (CCIE) DOS in the wide ranges of density, but cannot be fitted by using single Gaussian and un-cutting exponential-type DOS. Instead of the Gaussian and pure exponential DOSs, the CCIE DOS is recommended. In this work, we use the Gaussian and CCIE DOSs to calculate the GER. The results obtained from the CCIE DOS are very different from that of the Gaussian DOS. And we also analyze the data of ideality factors extracted by Wetzelaer et al. [34]. Our analysis shows that the data of ideality factors can also be explained by an extended *J-V* equation of organic diodes based on the GER.

2. Theoretical formalism

Ashcroft and Mermin firstly [12] proposed the fundamental formulae of GER:

$$\frac{D}{\mu} = \frac{p}{q}\left(\frac{\partial p}{\partial E_F}\right)^{-1} \equiv \zeta\frac{kT}{q} \tag{4}$$

where E_F is the quasi-Fermi level and p is the charge carrier density which can be written as: