Charge Transport in Organic Semiconductors

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1 Overview

In class, we have discussed the experimental observations regarding the temperature dependence of charge mobility in molecular and polymeric organic semiconductors. Different trends are observed for different classes of materials and in different temperature regimes. A number of models have been derived to describe these trends, including the band and band-like transport model, multiple trap and release (MTR), variable range hopping (VRH) theories, Bässler's Gaussian disorder model (BGD), percolation, mobility edge, Marcus-type charge transfer, and nuclear tunneling.

The paper of Liu *et al.*, upon which this reader is based, outlines existing models for transport in single crystal, polycrystalline and amorphous materials.[1]. A generalized Einstein relation for charge mobility in organic semiconductors is derived and shown to replicate the results obtained with multiple pre-existing models. These models had been developed to describe charge transport in materials with various degrees of disorder. By introducing a delocalization parameter (ΔD) and variance (ΔE) to tune the shape of the density of states, the authors demonstrate that it is also possible to replicate experimentally reported mobilities, including trends regarding the temperature- and gate-voltage-dependence of mobilities for a given material. In particular, for a given ΔE, it is shown that for most values of ΔD, the mobility increases as temperature increases, while at very high degrees of delocalization ($\Delta D \longrightarrow 1$), the carrier mobility increases with *decreased* temperature. This inverse temperature dependence is an indication of 'band-like' transport, as is the case for a small number of organic materials, such as C8-BTBT, naphthalene, rubrene, TIPS-pentacene, and the polymer IDTBT, while the direct temperature dependence is representative of a thermally-activated charge transport mechanism. Altogether, this model provides a holistic view of charge transport.

2 Einstein relations

To study the temperature dependence of the charge mobility, one must find an equation that relates the mobility μ of a charge q to the temperature T. Einstein equations provide such a relation. From the most general point of view, mobility in a semiconductor can be expressed by the following generalized Einstein relation:

$$\mu = \frac{qD}{n(E_F^*, T)} \frac{\partial n(E_F^*, T)}{\partial E_F^*} \tag{1}$$

where n is the charge carrier concentration and (E_F^*) is the quasi-Fermi energy, not the Fermi energy (E_F). By definition, the Fermi energy is the energy at which a corresponding state has a 50% probability of being occupied at thermal equilibrium. In a semiconductor with a fully occupied valence band and an unoccupied conduction band, E_F is located at the midway point between the edges of the conduction band and valence band (even though there may be no available state at that energy). The Fermi energy is therefore a material-dependent and constant value. When a voltage bias is applied on the semiconductor, the system is brought out of thermal equilibrium and the 'state' with a 50% occupation probability is no longer the one at the Fermi level but at the quasi-Fermi energy, given by:

$$E_F^* = E_F - qV(x) \tag{2}$$

We propose a demonstration of the generalized Einstein relation (1) in the following box.

The net current density J in a semiconductor is the sum of the drift (J_{drift}) and diffusion (J_{diff}) currents:

$$J = J_{drift} + J_{diff} \tag{3}$$

where J_{drift} is given by Ohm's law:

$$J_{drift} = q\mu nE \tag{4}$$

and J_{diff} is given by Fick's law:

$$J_{diff} = -qD\frac{\partial n}{\partial x} \tag{5}$$

in which n is the charge carrier density (described below), D is the diffusion coefficient, E is the electric field and x is the coordinate axis. At equilibrium, the total current is 0, therefore Eq. 3 can be rewritten as:

$$q\mu nE = qD\frac{\partial n}{\partial x} \tag{6}$$

The electric field E is the opposite of the derivative of the potential $V(x)$ with respect to x, which we replace accordingly on the left side. Given that the charge carrier concentration is a function of the quasi-Fermi energy, the quasi-Fermi energy is a function of the potential and that the potential is a function of x, we can apply the chain rule to the derivative on the right-hand side:

$$-q\mu n\frac{\partial V(x)}{\partial x} = qD\frac{\partial n}{\partial E_F^*}\frac{\partial E_F^*}{\partial V(x)}\frac{\partial V(x)}{\partial x} \tag{7}$$

By simplifying, we obtain

$$-\mu n = D\frac{\partial n}{\partial E_F^*}\frac{\partial E_F^*}{\partial V(x)} \tag{8}$$

The derivative of E_F^* with respect to $V(x)$ in Eq. 8 leaves us with $-q$. After rearranging, the Einstein relation therefore describes charge mobility in a semiconductor:

$$\mu = \frac{qD}{n(E_F^*, T)}\frac{\partial n(E_F, T)}{\partial E_F} \tag{9}$$

In the particular case of a crystalline, defect-free and non-degenerated semiconductor, the general Einstein relation simplifies into the classical (Einstein-Smoluchowski) form:

$$\mu = \frac{qD}{kT} \tag{10}$$

In the paper, Lui *et al.* establish a new form of a general Einstein relation, connecting the mobility to temperature-dependent parameters such as the diffusion coefficient, in the restricted case of disordered organic semiconductors.

3 Generalized Einstein relation in disordered organic semiconductors

The diversity of local environments surrounding each molecule in a bulk organic semiconductor leads to fluctuations of the molecular electronic states. Then, an appropriate way of describing the electronic structure of the semiconductors is to use the density of states (DOS, $N(E)$) which gives the number of electronic state at a given energy. In organic semiconductors this density of states is usually well-described by a Gaussian distribution:

$$N(E) = \frac{N_t}{\sqrt{2\pi}\Delta E} exp\left[- \frac{(E - E_0)^2}{2\Delta E^2} \right] \tag{11}$$

where ΔE is the variance of the DOS Gaussian and E_0 is the energy marking the center of the distribution. N_t is the 'characteristic' (*i.e.* material-dependent) band DOS.

The DOS is used, in combination with a distribution function $f(E,T)$ determining the probability of occupation of a state at the energy E at T, to calculate the charge carrier density n, which is then given by:

$$n = \int_{-\infty}^{+\infty} N(E) f(E,T)\, dE \tag{12}$$

The most commonly used distribution function to describe organic semiconductors is the **Fermi distribution**, which takes the following form:

$$f(E,T) = \left[1 + exp(\frac{(E - E_F^*)}{kT} \right]^{-1} \tag{13}$$

The shape of this distribution and its derivative are shown in Figure 1. We notice that at low temperatures, the distribution is essentially a step function, where the quasi Fermi level marks the boundary between fully occupied and unoccupied states. At higher temperature, the probability of occupation of a state above the quasi Fermi energy is no longer null, so if states exists in this region the conduction band is now partially filled while the valence band is partialy emptied. We note also that the lower the temperature, the closer to a delta function the derivative becomes.

On another hand, the conductivity at T which is defined as:

$$\sigma = qn\mu \tag{14}$$

can be calculated by the Kubo-Greenwood integral (which will not be demonstrated in this reader):

$$\sigma = \int_{-\infty}^{+\infty} \sigma'(E) \left[-\frac{\partial f(E,T)}{\partial E} \right] dE \tag{15}$$

where σ' is define as the energy-dependent conductivity, also named 'microscopic' conductivity and set as

$$\sigma'(E) = q^2 N(E) D(E) \tag{16}$$

By looking at the shape of the derivative of the Fermi distribution, it can be understood that the conductivity given by the Kubo-Greewood integral corresponds to the integration of the energy-dependent conductivity weighted by "the closeness of the energy level to the quasi Fermi level".

By rearranging the basic conductivity expression and then replacing σ and n by the expressions we have established for them, we arrive at the general Einstein expression in the case of disordered organic semiconductors outlined in the paper:

$$\mu = \frac{\sigma}{qn} = \frac{q \int_{-\infty}^{+\infty} N(E) D(E) \left[-\frac{\partial f(E,T)}{\partial E} \right] dE}{\int_{-\infty}^{+\infty} N(E) f(E,T)\, dE} \tag{17}$$

We have seen that the density of states in disordered organic semiconductors follows a Gaussian distribution as a consequence of disorder. Therefore, an electron on a tail state near the energy gap is more localized than in the center of the distribution, considering its surrounding available states, and the conductivity in the range of the tail state is necessarily lower. This attenuation can be mathematically described by assuming a similar Gaussian distribution to that employed for the energy-dependent density of states $N(E)$ for

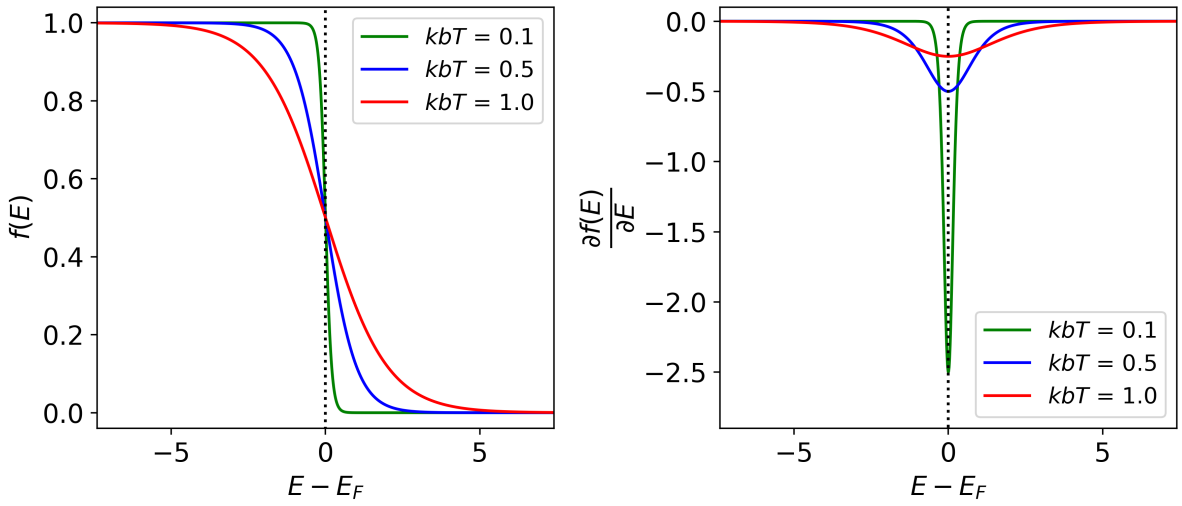

Figure 1: Shape of the Fermi distribution $f(E)$ (left) and the derivative of the Fermi distribution (right) as a function of the energy relative to the Fermi energy (shown as the dotted line), at three different temperatures. For more details, see `http://lampx.tugraz.at/~hadley/ss1/materials/thermo/gp/gp/Fermi-function.html`

the diffusivity at each energy $D(E)$:

$$D(E) = \frac{D_0}{\sqrt{2\pi}\Delta D} exp\left[- \frac{(E - E_0)^2}{2\Delta D^2} \right] \tag{18}$$

with D_0 a prefactor.

Leading then to a energy dependent conductivity as Gaussian distribution itself:

$$\sigma'(E) = \frac{\sigma_0}{\sqrt{2\pi}(\Delta D \Delta E)} exp\left[- \frac{(E - E_0)^2}{2(\Delta D \Delta E)^2} \right] \tag{19}$$

In this picture, ΔD is a dimensionless parameter describing the delocalization of states at the edge of the density of states. If ΔE is small, the states at the edges of the DOS have very low microscopic conductivity.

The expression of the energy-dependent density of states $N(E)$ and diffusivity $D(E)$ as Gaussian distribution are then used in this paper in the GER established (17) to study the mobility μ as a function of ΔE and ΔD.

References

[1] Chuan Liu, Kairong Huang, Won-Tae Park, Minmin Li, Tengzhou Yang, Xuying Liu, Lijuan Liang, Takeo Minari, and Yong-Young Noh. A unified understanding of charge transport in organic semiconductors: the importance of attenuated delocalization for the carriers. *Materials Horizons*, 4(4):608–618, 2017.