6.5 Towards a Unified View

Characteristic Features of Organic Semiconductors

- **Einstein-Smoluchowski relationship for a disorder-free, single crystalline semiconductor in the non-degenerate state (i.e., Boltzmann approximation)**

$$\mu = \frac{Dq}{kT}$$

- **for a disordered semiconductor in the degenerate state, the mobility becomes a function of the charge carrier concentration *n***

$$\mu = \frac{Dq}{n(E_f, T)} \frac{\partial n(E_F, T)}{\partial E_F}$$

- **density of states (DOS) has a narrow Gaussian distribution:**

$$N(E) = \frac{N_t}{\sqrt{2\pi}\Delta E} \, e^{-\frac{(E - E_0)^2}{2\Delta E^2}}$$

typical total DOS N_t = 10^{21} cm^{-1}; variance of Gaussian distribution $\Delta E = \sigma \leq 0.2$ eV; center of the DOS E_0

Liu, Noh, *Mater. Horizon* **2017**, *4*, 608; see also reader

Generalized Einstein Relation

- **Fermi-Dirac distribution for overall charge carrier density *n:***

$$n = \int_{-\infty}^{+\infty} N(E) f(E) dE = \int_{-\infty}^{+\infty} N(E) \frac{1}{1 + e^{\frac{E - E_f}{kT}}} dE$$

- **electronic states in band tails more localized than those closer to the center of the DOS; microscopic conductivity $\sigma'(E)$ and diffusivity $D(E)$ of states becomes energy-dependent:**

$$\sigma'(E) = q^2 N(E) D(E) = \frac{\sigma_0}{\sqrt{2\pi}\ \Delta D\ \Delta E} e^{-\frac{(E - E_0)^2}{2\ \Delta D\ \Delta E}}$$

- **Kubo-Greenwood integral for overall conductivity**

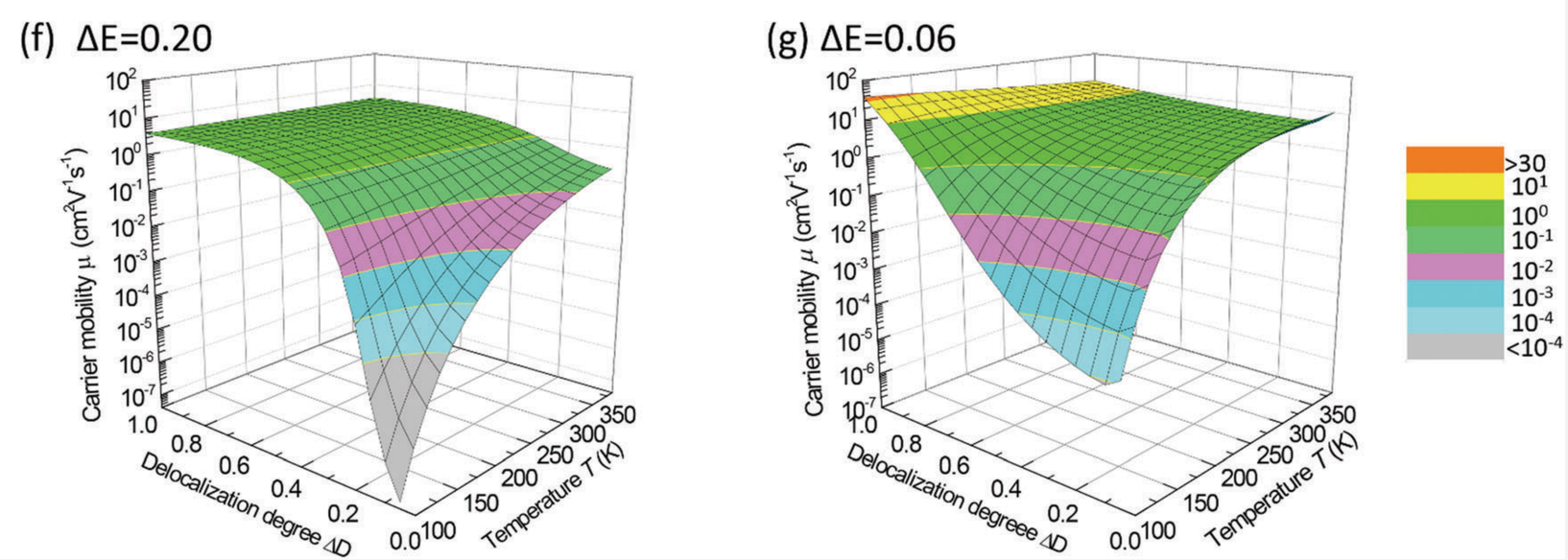
$$\sigma = -\int_{-\infty}^{+\infty} \sigma'(E) \frac{\partial f(E)}{\partial E} dE$$

- **Generalized Einstein Relation (GER)**

$$\mu = \frac{\sigma}{qn} = \frac{-q \int_{-\infty}^{+\infty} \sigma'(E) \frac{\partial f(E)}{\partial E} dE}{\int_{-\infty}^{+\infty} N(E) f(E) dE}$$

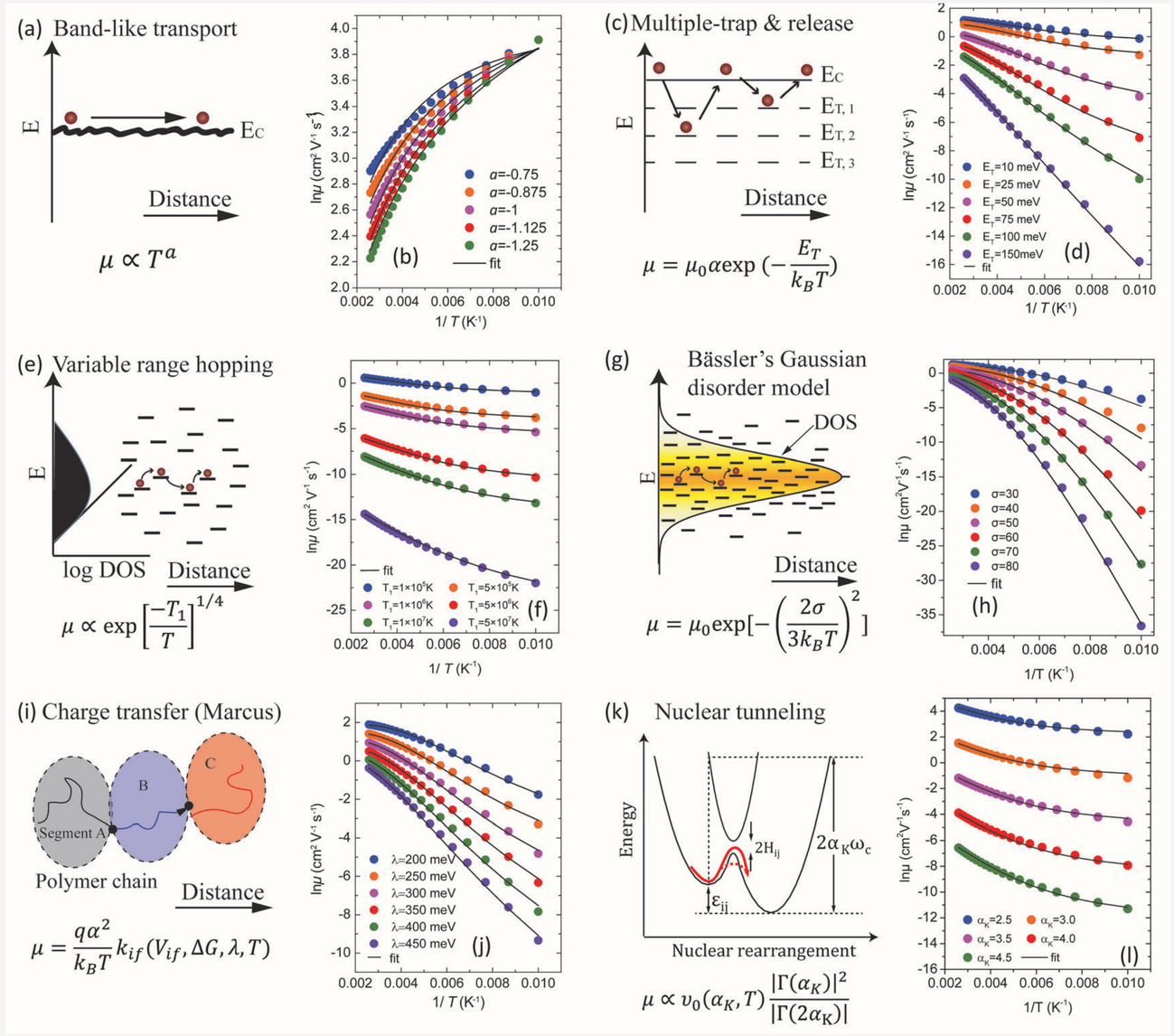
Universal View of Temperature Dependence

- delocalization degree ΔD (= 0–1) and variance of Gaussian distribution $\Delta E = \sigma$ determine energy landscape and transport mechanism



- **for low energetic disorder $\Delta E = \sigma$ and high degree of delocalization ΔD, a negative temperature dependence can be observed (band and band-like transport)**
- **for high energetic disorder $\Delta E = \sigma$ and/or low degree of delocalization ΔD, a positive temperature dependence can be observed (disorder control or polaron transport)**
- **diagonal movement in the diagram if degree of delocalization ΔD changes with temperature gives cross-over between transport regimes**

Unified Description of Various Transport Models



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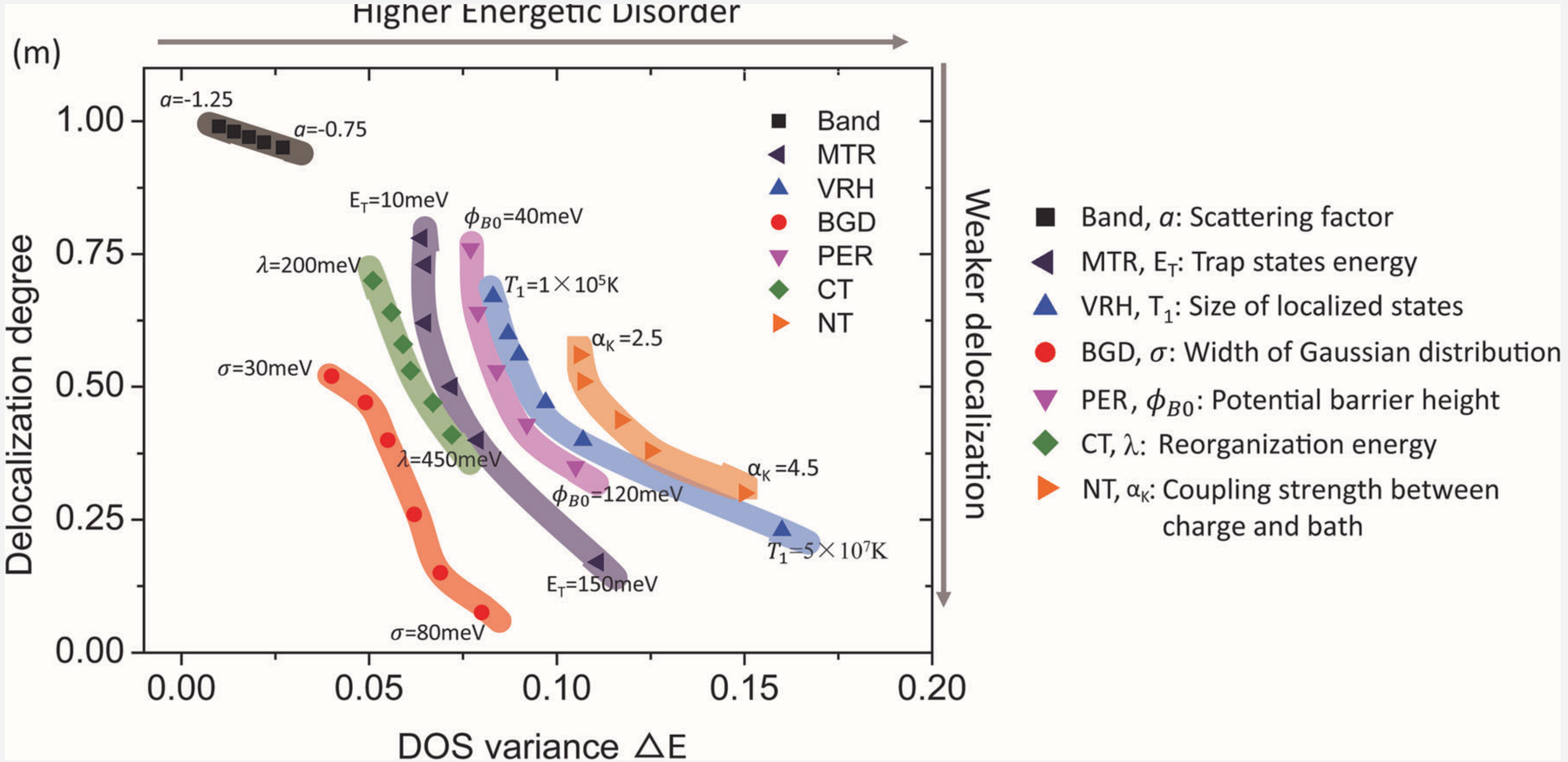
Unified Description of Various Transport Models



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A unified understanding of charge transport in organic semiconductors: the importance of attenuated delocalization for the carriers†

Chuan Liu,*[a] Kairong Huang,[a] Won-Tae Park,[b] Minmin Li,[a] Tengzhou Yang,[a] Xuying Liu,[c] Lijuan Liang,[cd] Takeo Minari[c] and Yong-Young Noh *[b]

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The variety of charge transport theories for organic semiconductors (OSCs) raises the question of which models should be selected for each case, and there is a lack of generalized understanding regarding various OSCs over the full range of crystallinity from single crystal to amorphous. Here, we report that the generalized Einstein relation (GER) can unify various theoretical models and predict charge transport in OSCs with various crystallinities, by altering the variance of the density of states and the delocalization degree in a Gaussian-distributed density of states. The GER also provides a good fitting to much of the experimental data of temperature- and gate-voltage-dependent mobility for different OSCs in transistors. Consequently, disorders of charge transport in various OSCs can be directly compared in the same map, which reveals how energetic disorder and the delocalization degree determine charge transport in organic devices.

Conceptual insights

Different classes of organic semiconductors (OSCs) have been described by various charge transport mechanisms from a model of band transport to variable range hopping, according to the molecular structure and crystallization. There is a lack of consensus in describing, predicting, and comparing transport in OSCs. This work describes a new understanding in charge transport, the generalized Einstein relation (GER), which unifies several classic theories for transport dynamics. By defining the variance in the density of states and delocalization degree, the GER predicts well the experimental data of a broad range of OSCs with various crystallinities, including temperature- and gate-voltage-dependent mobility data in transistors. The results are sufficiently general to allow a direct comparison of disorder factors in charge transport and provide guidelines to understand how energetic disorder and localization determine the electric characteristics of organic devices.

1. Introduction

Recently, many new organic semiconductors (OSCs) have been reported to exhibit high field-effect mobility ($>10\ cm^2\ V^{-1}\ s^{-1}$),[1] despite the morphology of some thin films not being highly crystalline.[2] For example, it is difficult to predict the charge transport properties through checking the crystallinity of state-of-the-art donor–acceptor (D–A) conjugated polymers by X-ray-based structural analysis tools as many of them exhibit a low crystallization degree or possess a non-crystalline nature.[3] New types of methods need to be developed to further understand the charge transport of these new OSCs, and a general consensus is still far from being reached, especially for those OSCs with high structural disorder but with superb mobility.[4] Unlike single-crystals, the abundant structural defects and strong lattice vibrations owing to the weak van der Waals interactions are inherent in OSCs and result in complicated transport mechanisms,[5] which lead to the dependence of the mobility on the temperature and/or the carrier concentration.[6]

Up to now, different theories concerning microscopic charge transport mechanisms have been proposed and many of them have been supported by evidence in different experiments on the temperature dependence of carrier mobility with various materials.[4a, 5a, 6b] A brief summary of charge transport theories is given in Fig. 1, in which the theories are roughly classified according to the crystallinity or the structural disorder of the semiconductors: (1) classic band-like transport is expected for disorder-free OSCs, which are mainly single crystalline materials[7] or some conjugated polymers with extremely low torsions of chains.[8] (2) For polycrystalline OSCs with a low extent of structural disorder, the mobility edge model is applicable and it is similar to the multiple trap and release (MTR) model.[6b,9] (3) In amorphous or highly disordered semiconductors, charge transport mainly occurs by hopping or tunneling among localized

[a] State Key Laboratory of Optoelectronic Materials and Technologies and the Guangdong Province Key Laboratory of Display Material and Technology, School of Electronics and Information Technology, Sun Yat-sen University, Guangzhou 510275, China. E-mail: liuchuan5@mail.sysu.edu.cn
[b] Department of Energy and Materials Engineering, Dongguk University, 26 Pil-dong, 3 ga, Jung-gu, Seoul 100-715, Republic of Korea. E-mail: ynoh@dongguk.edu
[c] International Centre for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan
[d] Beijing Institute of Graphic Communication, Beijing 102600, China
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Charge Transport in Organic Semiconductors

Lucile Chassat - Jacob Terry Blaskovits

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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:

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