

APPLICATION FOR 2015 DEIS GRADUATE FELLOWSHIP

**First principles computation of  
carrier mobilities in polymeric insulators**

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## 1. Introduction

Polymeric insulators are extensively used in high voltage applications. In order to improve the reliability, durability, operating voltage, compactness, cost-efficiency and functionality of electric power equipment and transmission cables, it is necessary to understand the aging process of polymeric insulators. Although it is widely accepted that degradation of polymers are correlated with space charge which is formed in the material [1,2], there remains a lack of understanding of charge transfer (CT) phenomena, despite extensive experimental efforts. One of the most fundamental parameters required to understand CT is charge carrier mobility of the material. Unfortunately, we are still far from computing charge carrier mobility in polymeric insulators without any ad hoc assumptions or parameters; moreover we can hardly discuss qualitative characteristics of mobilities in most electrically insulating materials. This is partly due to the fact that although CT in solids is intrinsically quantum mechanical, we were unfamiliar with such treatment.

## 2. State of the art

### 2.1. Quantum mechanical studies on electronic states in PE

Since the beginning of the 21st century, *first principles calculation*\* has been utilized to clarify the nature of CT in polyethylene (PE) [3-12]. The achievements can be summarized as follows:

- Charge carrier traps in PE are characterized from atomistic point of view; *Physical trap*<sup>†</sup> energies are of the order of 0.1 eV and the depth of *chemical traps* range between 0.1 to 3 eV, depending on the chemical structure, e.g. conjugated double bond, carbonyl, vinyl, and so on [3-11]. This is confirmed among oligomers of PE [3-5], core-shell structure [6-8] and amorphous and lamella like structure [9,10].
- Increase in conductivity of PE upon iodine doping is discussed qualitatively; It is concluded that increase in hole mobility is due to the mixed impurity states, which facilitates inter-chain hole transfer [11].
- Electronic state of excess electron in crystal PE is studied by computing the wave function of the conduction-band edge; Wave function of conduction-band shows an inter-chain character while the valence-band state shows intra-chain character. [12].
- Current-voltage characteristic of electron in PE is predicted from the density of states, which is computed by first principles method; note that phenomenological models and empirical parameters are used [13].
- Mobilities of excess electrons in disordered *n*-alkanes (oligomers of PE) are evaluated; note that semi-empirical parameters are utilized to describe interactions between excess electrons and molecules [14].

In short, (1) qualitative picture of impurity- and defect-limited CT in PE has been revealed, (2) quantitative values which can be inserted into phenomenological models are computed, and (3) electron mobilities in defect-free *n*-alkanes are computed with the aid of semi-empirical parameters.

### 2.2. Computation of mobilities in organic “semiconductors”

Although there is not much first principles studies related to insulating materials, charge carrier mobilities in organic “semiconductors” have been extensively studied [15-17]. Significant feature of CT in most organic materials is that holes and electrons are localized in the molecules and exhibit a hopping conduction. Hopping conduction in organic semiconductors are evaluated by computing the CT rate between molecules from first principles calculations by means of Marcus equation, which can be explicitly derived from the well-known Fermi’s Golden rule, i.e. Ad hoc assumptions or parameters are **NOT** used in this approach. Computed CT rates are used to solve the differential master equation in order to study charge transfer. Mobilities in semiconducting crystals and amorphous of small molecules has been vastly examined within this frame work. Moreover, **although not authorized nor fully established**, strategies to evaluate mobilities of amorphous, crystalline and semi-crystalline polymeric semiconductors have rapidly evolved over the last few years, and thereby revealed qualitative nature of CT in polymers to a certain extent [18-25].

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\* First principles approaches, i.e. *ab initio* methods and density functional theory (DFT) methods, basically solve the Schrödinger equation by introducing several approximations. Due to the huge computational costs of *ab initio* methods, computation of large systems are usually done by DFT methods.

<sup>†</sup> Physical traps are due to conformational disorder of molecules.

### 3. Proposed Work

#### 3.1. Motivation

As mentioned in the previous chapter, quantum mechanical studies on electronic states in PE have provided us insight into the nature of CT in PE. However, it should be emphasized that most studies still remain qualitative, or requires (semi-)empirical parameters. In addition, existing models such as Gaussian disordered hopping model and computational methods cannot account for various experimental results such as the *time-dependent mobility* ‡. On the other hand, studies on polymeric semiconductors have revealed that in order to account for *time-dependent mobilities*, i.e. in order to quantitatively account, in a unified manner, for mobilities of polymers, it is necessary to take into consideration the morphology of polymers and compute atomistic values such as intra- and inter-molecular charge hopping rates.

#### 3.2. Goal of this project

Considering the above, the ultimate goal of this research is to establish a computational model, which is capable of simulating carrier mobilities of polymeric insulators including various defects, impurities, additives and (nano)composites. The model will be built from an atomistic perspective, and without any ad hoc parameters. This will allow us to understand the physical basis of CT, which will serve as a basis for further discussion on aging or breakdown of the material. In addition, the relation between atomistic structures and macroscopic characteristics will enable us to tailor various properties of polymeric insulators. The goal of this project in particular is to compute the “time-, electric field-, temperature-dependent mobilities” of polymeric insulators with and without defects and impurities.

#### 3.3. Computational Methods

The overview of our computational strategy is shown in Fig. 1. As shown in Fig. 1,

- (1) Morphologies of polymeric insulators are obtained by molecular dynamics (MD). When the meso-scale structures are required, we will adopt the coarse graining technique to enable MD simulations at longer time and length scales (Fig. 1 (I)).
- (2) All arbitrary pairs of molecules, namely dimers, are taken from the structure obtained by MD simulations. In order to compute hopping rates between these dimers, transfer integral, reorganization energy and free energy difference are computed by means of first principles calculation, and are inserted into the well-known Marcus formula. (Fig. 1 (II)).
- (3) Given the coordination of carrier sites and hopping rate between these sites from procedure (1) and (2), respectively, kinetic Monte Carlo (KMC) simulation is applied to simulate the motion of charge carriers. For diffusive process, the mobilities of carriers are determined with a combination of mean square displacement of carrier and Einstein relations (Fig. 1 (III)). It should be noted that electric field dependence of carrier mobilities can be evaluated by simulating time-of-flight (TOF) experiment. In this case, energy difference due to external electric field  $-eE \cdot \Delta r$  is added to the inherent free energy difference  $\Delta G^0$  in the Marcus formula (Fig. 1 (II)).

### 4. Preliminary computations (Confirming the validity of our strategy.)

#### 4.1. Hole mobility in PE ([C1] to be presented at 2015 CEIDP, Session 1, 1-1 (preliminary program))

As shown in Fig. 2, we have computed hole mobility in crystal PE. It is shown that (i) hole transfer in PE occurs in a “hopping regime”, (ii) hole mobilities of oligomers of PE are smaller compared to polycyclic aromatic hydrocarbon (PAH) both due to small transfer integral and large reorganization energy. In addition, we have shown that (iii) carbonyl impurity may well increase hole mobility due to the increase of transfer integral while (iv) hole mobility in amorphous region decrease due to the increase of reorganization energy and free energy difference, i.e. increase of activation energy.

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‡ Time-dependent mobility: Experimental results show that the mobility at short length/time scale is smaller by several orders of magnitude compared with those at long length/time scale. This is observed both in semiconductors [24] and insulators [26].

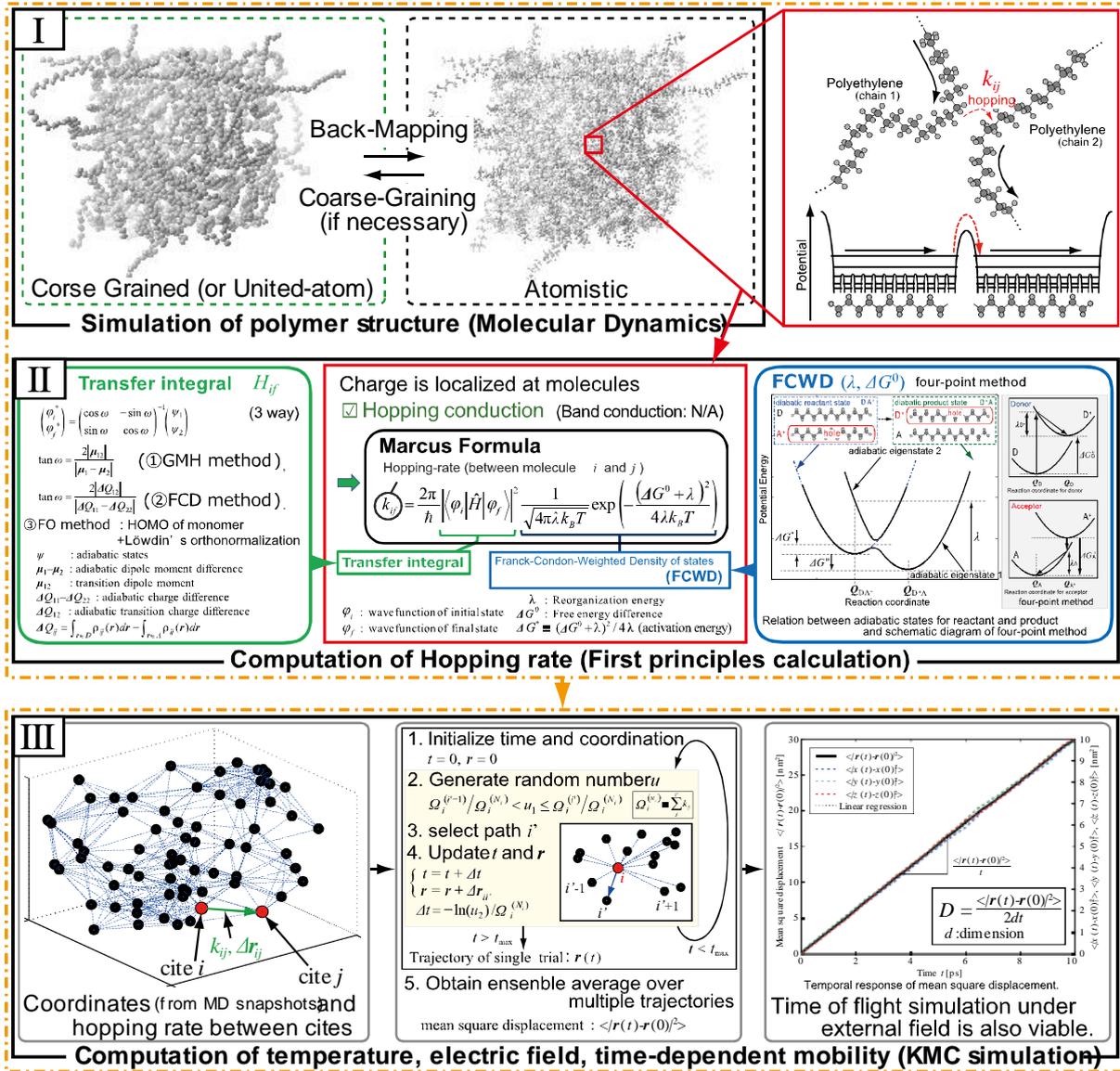


Fig. 1 Schematic diagram of three-step procedure for determining temperature-, electric field-, and time-dependent mobilities of polymeric insulators. In order to test the robustness of our results, transfer integral is evaluated in three ways: general Mulliken-Hush (GMH) method [27], Fragment charge difference (FCD) method [28] and fragment orbital (FO) method [29]. Reorganization energy and free energy difference are computed by means of four-point method [30]. For KMC simulation, we have adopted a standard procedure proposed by Bortz [31]. In addition to the procedure explicitly described in this figure, we are intending to compute hopping rates between cites in a single molecule; static disorder of a polymer chain localizes the molecular orbital whereby generating multiple charge hopping cites in a single molecule.

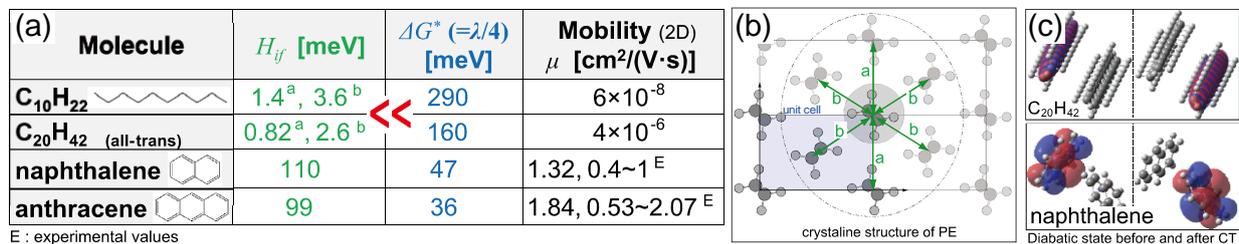


Fig. 2 Computation of hole mobility of PE at 300K: (a) computed values of transfer integral, activation energy and mobility of alkane (here in after PE) and polycyclic aromatic hydrocarbon (PAH), (b) crystalline structure of PE and (c) charge localized states before and after hole transfer, which is estimated with GMH method. Computed and experimental values for PAH are taken from Refs. [32] and [33-36], respectively. (i) It is clearly seen for PE that transfer integral is by two orders of magnitude smaller than reorganization energy. This strongly indicates that hole transfer in PE occurs in a “hopping regime”<sup>8</sup>. (ii) Transfer integral of PE is by two orders of magnitude smaller than that of PAH, on the other hand, activation energy of PE is larger compared to that of PAH, both of which contribute to small mobility of PE. (iii) It was shown that these differences are due to orbital type differences:  $\pi$ -type orbital of PAH are delocalized to some extent thereby results in large coupling between the neighboring orbitals, and  $\sigma$ -type orbitals of PE has strong contribution to the covalent chemical bond and therefore resulting in large reorganization energy of PE. Experimental lattice constants [37] of crystalline structure were used to arrange PE chains.

<sup>8</sup> Classification of conduction process: completely localized (1.  $H_{ij}=0$ ), weakly coupled, localized (2.  $|H_{ij}| < \lambda$ ), strongly coupled, delocalized (3.  $|H_{ij}| > \lambda$ ) [38,39].

## 4.2. Charge mobility in liquid benzene

In order to confirm that mobilities of disordered system can be obtained by the combination of MD and KMC simulations (Fig. 1 (I, III)), we have computed the electron mobility of liquid benzene (Fig. 3). It is clearly seen from Fig. 3 that the computed value of electron mobility is in excellent agreement with experimental results for wide range of temperature and pressure.

## 5. Work program

It is obvious from these results that our computational strategy is valid for describing hole and electron mobilities in crystalline polymers and amorphous small molecules. Thus we will (1) compute mobilities of various crystalline polymers and answer to frequently asked questions such as why hole mobilities larger than electron mobilities in some materials and what defines the activation energy, (2) compute “time-dependent mobilities” in disordered polymers via modifying the existing model; simulate TOF measurements including intra-molecular carrier hopping rate, and we will evaluate the effect of defects and impurities on carrier mobilities. I declare that significant findings will be presented at IEEE DEIS-sponsored conferences (IEEE CIEDP and IEEE ICD). In addition, we will submit some papers to IEEE TDEI.

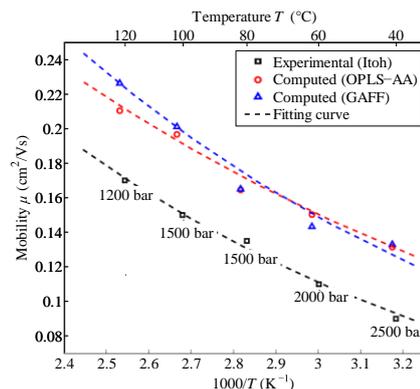


Fig. 3 Computed values of electron mobility in liquid benzene under various temperature and pressure. OPLS-AA and GAFF force fields were used for comparison. Experimental values are taken from Ref. [40]. We have confirmed that effect of dynamic disorder (thermal fluctuation of transferintegral) is negligible.

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