Non-equilibrium thermodynamics of charge separation in organic solar cells

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This work presents the first theoretical description of the non-equilibrium thermodynamics of charge separation in organic solar cells. Based on the concept of stochastic thermodynamics, we connect the kinetics of charge transport with the thermodynamic properties to address the non-equilibrium nature of charge separation. The impacts of disorder, permittivity, and electric field on the free energy difference are investigated as showcases, to demonstrate the capability of the developed method.

Introduction - Despite years of research on the fundamental properties of organic solar cells one of the most essential aspect is still not fully understood: what causes the efficient dissociation of charge transfer (CT) states into free charge carriers despite the presence of the strong Coulomb attraction? Various physical properties have been proposed to promote CT separation. Delocalized charge carriers can efficiently escape their strong binding energy and enhance the CT-dissociation efficiency due to a larger initial separation [14]. "Hot" CT states are considered providing a sufficient initial excess energy to overcome the binding energy [5–8]. Previous publications have suggested that the interplay of entropy with both the dimensionality of the semiconductor and the disorder in molecular orbital energies can lead to a strong decrease of the separation barrier [9–13]. Gregg studied the relation of dimensionality and entropy based on the degeneracy of states \( W \) as a function of the separation distance \( r \) using the equilibrium relation \( \Delta S(r) = k_B \ln W(r) \) [10]. In semiconductors with higher dimensionality, the free energy barrier is significantly reduced due to the strong increase in available states. Hood et al. emphasized that the above approach can capture the ordered case, but it underestimates the entropic contribution to the free energy in case of energetically disordered states [9]. To account for the energy of the states, Hood et al. used an improved measure for the free energy difference based on the canonical partition function [9]. The partition function is purely based on the difference of the initial and final energies of the electron-hole pair and the degeneracy of final configurations after separation. Following this equilibrium approach, an increase in disorder \( \sigma \) strongly reduces the energetic barrier and proposes spontaneous charge separation for \( \sigma \geq 100 \text{ meV} \). However, it is known that a large disorder can hamper charge transport and thus can lead to significant charge trapping. Additionally, an increased disorder may impact the recombination rate of the CT states. This can be directly seen from the energy-gap law [14] [15], which reveals an increase in non-radiative recombination for a decrease in CT energy \( E_{\text{CT}} \). Existing thermodynamic descriptions are not appropriate for describing the non-equilibrium nature of the separation process [13] [16]. Giazitzidis et al. approached a non-equilibrium description by correcting the equilibrium free energy using the distribution in space of the electron-hole pair evaluated from Monte Carlo simulation [16]. Shi and coworkers emphasized that the disorder-enhanced dissociation is a non-equilibrium effect and associated the average energy of the electron-hole pair along a dissociation path with the free energy difference [13].

Despite the progress in understanding the thermodynamics of charge separation, no non-equilibrium thermodynamic description of the charge separation is present to date. In this work, we establish the first link between the kinetics of charge separation and its fundamental non-equilibrium thermodynamic properties based on the concept of stochastic thermodynamics. Free energy differences and entropic contributions are obtained from the kinetic rates, which fulfill the detailed balance [17], and the Jarzynski relation for the free energy difference [18] [19]. Using kinetic Monte Carlo (kMC) simulations, free energy differences of the charge separation are computed based on the stochastic description of particle trajectories. The presented method is finally used to study the role of the energetic disorder, the permittivity, and the reorganization energy on the free energy difference.

Theory - The relation between the work \( W \) performed on a system to change the system state and the associ-
ated Helmholtz free energy difference $\Delta F$ between the initial and the final state provides significant insight into the thermodynamics of the state transition. If the system state changes infinitely slow, the Helmholtz free energy will equal the total work: $W = \Delta F = F^B - F^A$, where $F^B/A$ refers to the equilibrium free energy in the final/initial state. If the system change occurs on a finite rate, $W$ depends on the initial microscopic conditions of the system and the reservoir, which results in:

$$\langle W \rangle \geq \Delta F.$$  

(1)

If $\langle W \rangle - \Delta F > 0$, the difference is the dissipated work $W_{\text{diss}}$ which is associated with an increase in entropy during the state transition.

A fundamental step towards the thermodynamic description of non-equilibrium processes has been done by Jarzynski \[18\[19\]. The main result connects the work with the difference in Helmholtz free energy by an equality:

$$\exp(-\beta W) = \exp(-\beta \Delta F).$$  

(2)

This seminal result links the equilibrium information $\Delta F$ with an ensemble of non-equilibrium trajectories $z_{0\to N}$ between the initial and the final state. Here, we describe briefly how to obtain above properties from the kinetic Monte Carlo formulation of the charge separation process (schematically depicted in Fig. 1).

We express the left hand side of Eq. (2) by an ensemble average over different trajectories $z_{i\to f}$. The kMC method computes a trajectory by a sequence of discrete system changes in phase space: $z_{0\to N} \to z_0, z_1, \ldots, z_N$, where $z_i$ is one state in the trajectory phase space. A probability $p(z_i|z_j)$ for the discrete transition from state $z_i$ to $z_j$ can be assigned by the ratio between the transition rate $a_{i\to j}$ and the sum of transition rates $a_{i\to k}$ to all available destinations $k$ in phase space:

$$p(z_i|z_j) = \frac{a_{i\to j}}{\sum_{k} a_{i\to k}}.$$  

(3)

The probability of the full trajectory $z_{0\to N}$ is given by

$$p(z_{0\to N}) = p(z_0)p(z_1|z_0)p(z_2|z_1)\cdots p(z_N|z_{N-1}),$$  

(4)

with the probability $p(z_0)$ to start in $z_0$. The initial CT state within OPVs depends on the interface properties between the donor and acceptor as well as the dynamical properties of excitons. One approach to capture the probability distribution for the initial condition is based on the partition function of the canonical ensemble:

$$p(z_0) = Z_0^{-1} \exp(-\beta E_0),$$  

(5)

with $\beta = (k_B T)^{-1}$, the Boltzmann constant $k_B$ and temperature $T$, and the initial system energy $E_0$. For the sake of simplicity, we always start the electron-hole pair at ideal energy levels without a disorder. Under this assumption the exact value of $p(z_0)$ only results in a shift in the free energy difference, thus we set $p(z_0) = 1$. Exciton dynamics and separation are neglected to focus on the thermodynamics of charge separation.

Now we can replace the left hand side of Eq. (2) by a trajectory ensemble average:

$$\langle \exp(-\beta W) \rangle = \sum_{z_{0\to N}} p(z_{0\to N}) \exp(-\beta W_{m}),$$  

(6)

where the sum is taken over all trajectories $z_{0\to N}$ from the initial to the final state with work $W_m = E_{\text{final}} - E_{\text{init}}$.

To obtain the free energy difference $\Delta F(r)$ for the electron-hole separation distance $r_{\text{eh}}$, we compute the trajectory until $r_{\text{eh}} > r$ for 500,000 electron-hole pairs.

We set up a simple kMC model of a $50 \times 50 \times 50$ nm$^3$ large 3-dimensional bilayer structure consisting of an acceptor ($z = 1 : 25$ nm) and a donor region ($z = 26 : 50$ nm). An electron-hole pair is initialized in the middle of the simulation box by placing the electron on the acceptor site and the hole on the adjacent donor site. We now compute the hopping rate of both charge carriers using the Marcus transfer theory \[20\],

$$a_{i\to j} = \frac{|V_{ij}|^2}{\hbar} \sqrt{\frac{4\pi}{\lambda}} \exp\left(-\frac{\beta(\Delta E_{ij} + \lambda)^2}{4\lambda}\right),$$  

(7)

with the charge transfer integral $V_{ij}$ between sites $i$ and $j$, reorganization energy $\lambda$, and the difference in energy $\Delta E_{ij}$. The kMC algorithm is based on Gillespie’s implementation \[21\] and summarized in our previous work \[22\].

Results - We investigate the free energy difference for the charge separation process using a simple bilayer structure. Initially, electron and hole are placed at neighboring sites in the acceptor and donor, respectively. Then, we perform kMC simulations of the separation of the electron-hole pair to obtain the free energy difference using the presented formalism. For both charge carriers we choose values typical for small molecules of $\lambda = 0.3$ eV and $V_{ij} = 1$ meV \[23\], respectively, and set $T = 300$ K. Note that the assumed isotropic transfer integral does only affect the charge separation time but not the free energy difference. We analyze the impact of the energetic disorder $\sigma$ and the permittivity $\epsilon_r$, as well as the role of an electrical driving field on $\Delta F$.

Figure 2 shows the free energy difference in dependence on the electron-hole distance $r_{\text{eh}}$ for a wide range of energetic disorders $\sigma = 0$ to 100 meV. The slope in $\Delta F$ is an indicator of the charge separation efficiency: a negative slope is representative for a spontaneous process, while an additional driving force is needed to separate the electron-hole pair in the presence of a positive slope. For $\sigma < 50$ meV, $\Delta F$ increases directly with rising $r_{\text{eh}}$. With increasing $\sigma$, $\Delta F$ drops immediately at even low-est distances before increasing slowly. The presence of the energetic disorder allows the charge carriers to disperse within a small distance by finding sites with favorable energy levels. However, after relaxation into favorable states close to their initial position, they need to
overcome large energy barriers arising from the strong Coulomb interaction and the disorder itself. Thus, in the absence of any driving force, a high energetic disorder favors an initial relaxation of the electron-hole pair to low energetic sites but hampers the escape from their Coulomb attraction. The latter statement is contradicting the observations made by Hood and Kassal [9], who claimed that the free energy is dropping continuously with increasing separation \( r_{eh} \). However, the trajectory the charge carriers need to cross to reach \( r_{eh} \) was not considered in their study and is of fundamental importance. For \( \sigma = 50 \text{ meV} \) an efficient separation is expected due to the slow increase in \( \Delta F \) for \( r_{eh} \geq 3 \text{ nm} \).

Several studies raised the importance of the permittivity \( \epsilon \) on the separation efficiency in OPVs [21–26]. We analyze the role of the permittivity on \( \Delta F \) in Fig. 3 by changing \( \epsilon \) down to a value of 3 at constant \( \sigma = 50 \text{ meV} \). At \( \epsilon = 3 \), the electron-hole pair needs to overcome a large energy barrier to be separated. This is due to the strong Coulomb interaction which coincides with a low separation probability. With rising \( \epsilon \) the barrier is strongly reduced, and an initial separation over some sites can occur easily at low energetic cost. Even an increase in permittivity to \( \epsilon = 4 \) can reduce the barrier in \( \Delta F \) significantly without the need of an external driving force. Thus, materials with permittivities above \( \epsilon \approx 4 \) can provide sufficient charge separation at operating conditions.

So far, we studied the charge separation process without any applied electric field (\( F_{ext} = 0 \text{ V/m} \)). This corresponds to the open-circuit condition within solar cells. However, during the operation of OPVs, an electric field driving the charge carriers towards the electrodes is present. To study the role of the driving force, we apply an additional linear potential drop along the \( z \)-axis and study the change in free energy difference (Fig. 4). With an increase in \( F_{ext} \) the free energy difference decreases as expected compared to the open-circuit condition. For \( F_{ext} \geq 2 \times 10^7 \text{ V/m} \), the barrier in \( \Delta F \) vanishes fully and even a full inversion is observed. This leads to an efficient separation of charge carriers. An external field of \( 10^7 \text{ V/m} \) is close to the short-circuit condition in OPVs, while lower fields (maximum power point in OPVs) only slightly lower \( \Delta F \). Note that this does not capture the complexity of the charge separation within bulk-heterojunction OPVs as the interface between donor and acceptor usually is not vertical to the electric field.

The large advantage of the presented concept is that the thermodynamic properties account for the energy dependence of the kinetic processes within the system of interest. As we describe the separation of the electron-hole

FIG. 2. Impact of the energetic disorder \( \sigma \) on the free energy difference \( \Delta F \) in dependence on the electron-hole separation distance \( r \) with \( \epsilon = 5 \). \( \sigma \) is varied from 0 to 100 meV. Solid lines are fitted to the data points. Error bars indicate the standard deviation in \( \Delta F \).

FIG. 3. Free energy difference in dependence on the electron-hole separation distance \( r \) for different permittivities \( \epsilon \) at \( \sigma = 50 \text{ meV} \).

FIG. 4. Free energy difference in dependence on the electron-hole separation distance \( r \) over the separation distance with changing \( F_{ext} \) for \( \sigma = 50 \text{ meV} \), \( \lambda = 300 \text{ meV} \) and \( V_{ij} = 1 \text{ meV} \).
pair by a Marcus electron transfer rate, we investigate the role of the transfer integral $V_{ij}$ and the reorganization energy $\lambda$. As mentioned previously, in an isotropic system with equal transport properties for both charge carriers $V_{ij}$ only scales the magnitude of all hopping rates, but does not impact the energy dependencies. The role of $\lambda$ on the difference in free energy is analyzed in Fig. 5. We observe no significant difference over a broad range from 50 - 400 meV. Note that one enters the inverted regime for larger $\sigma$ and lower values of $\lambda$ which usually is not the case for OPVs and thus is neglected.

**Conclusion** - To conclude, this Letter presents the first theoretical concept for the study of thermodynamic properties of the charge separation process based on a purely non-equilibrium description. We combine the Jarzynski free energy relation obtained from stochastic thermodynamics with kinetic Monte Carlo simulation of the charge separation to derive the free energy difference $\Delta F$. kMC simulations are used to compute energetics and probabilities of single trajectories of electron-hole pairs during the separation process. Based on the ensemble average on a large set of trajectories, we analyze $\Delta F$ for a range of energetic disorders, permittivities, reorganization energies, and external driving fields. Our results indicate that the presence of an energetic disorder favors the initial charge separation by relaxation to favorable energy states but at the same time hampers the escape from their Coulomb attraction. Energetic disorders of $\sigma \approx 50$ meV represent the best combination of initial charge relaxation and low free energy barrier. Moreover, an increase in permittivity significantly reduced the free energy barrier. With the presented non-equilibrium description of charge separation we overcome the shortcomings of existing (equilibrium) studies and connect the kinetics with the thermodynamic properties of the charge separation.

**Acknowledgement** - We acknowledge the TUM International Graduate School of Science and Engineering (IGSSE) by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) for funding.

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[1] F.-J. Kahle, C. Saller, S. Olthof, C. Li, J. Lebert, S. Weiß, E. M. Herzig, S. Hüttner, K. Meerholz, P. Strohciegl, et al., J. Phys. Chem. C 122, 21792 (2018).
[2] C. Deibel, T. Strobel, and V. Dyakonov, Phys. Rev. Lett. 103, 036402 (2009).
[3] S. Tschueuschner, H. Bäßler, K. Huber, and A. Köhler, J. Phys. Chem. B 119, 10359 (2015).
[4] V. Jankovic and N. Vukmivoric, J. Phys. Chem. C 122, 10343 (2018).
[5] A. A. Bakulin, A. Rao, V. G. Pavelevyev, P. H. van Loosdrecht, M. S. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne, and R. H. Friend, Science 335, 1340 (2012).
[6] H. Bäßler and A. Köhler, Phys. Chem. Chem. Phys. 17, 28451 (2015).
[7] G. Granconi, M. Masiuri, D. Fuzzi, A. Petrozza, H. Egelaaf, D. Brida, G. Cerullo, and G. Lanzani, Nat. Mater. 12, 29 (2013).
[8] M. L. Jones, R. Dyer, N. Clarke, and C. Groves, Phys. Chem. Chem. Phys. 16, 20310 (2014).
[9] S. N. Hood and I. Kassal, J. Phys. Chem. Lett. 7, 4495 (2016).
[10] B. A. Gregg, J. Phys. Chem. Lett. 2, 3013 (2011).
[11] T. M. Clarke and J. R. Durrant, Chem. Rev. 110, 6736 (2010).
[12] A. Gluchowski, K. L. Gray, S. N. Hood, and I. Kassal, J. Phys. Chem. Lett. 9, 1359 (2018).
[13] L. Shi, C. K. Lee, and A. P. Willard, ACS Cent. Sci. 3, 1262 (2017).
[14] J. Benduhn, K. Tvingstedt, F. Piersimoni, S. Ullbrich, Y. Fan, M. Troiano, K. A. McGarry, O. Zeika, M. K. Riede, C. J. Douglas, et al., Nat. Energy 2, 17053 (2017).
[15] M. Azzouzi, T. Kirchartz, and J. Nelson, Trends Chem. (2019).
[16] P. Giazitzidis, P. Argyrakis, J. Bisquert, and V. S. Vikhrenko, Org. Electron. 15, 1043 (2014).
[17] T. Kirchartz and U. Rau, Phys. Status Solidi A 205, 2737 (2008).
[18] C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997).
[19] C. Jarzynski, Phys. Rev. E 56, 5018 (1997).
[20] R. A. Marcus, Rev. Mod. Phys. 65, 599 (1993).
[21] D. T. Gillespie, J. Phys. Chem. 81, 2340 (1977).
[22] W. Kaiser, J. Popp, M. Rinderle, T. Albes, and A. Gagliardi, Algorithms 11, 37 (2018).
[23] C. Poelking, K. Daoulas, A. Troisi, and D. Andrienko, in P3HT Revisited–From Molecular Scale to Solar Cell Devices (Springer, 2014) pp. 139–180.
[24] S. Y. Leblebici, T. L. Chen, P. Oalalde-Velasco, W. Yang, and B. Ma, ACS Appl. Mater. Interfaces 5, 10105 (2013).
[25] T. Albes and A. Gagliardi, Phys. Chem. Chem. Phys. 19, 20974 (2017).
[26] J. Brebels, J. V. Manca, L. Lutsen, D. Vanderzande, and W. Maes, J. Mater. Chem. A 5, 24037 (2017).