論 文 の 内 容 の 要 旨

論文題目　Mathematical Modeling of Morphology and Performance of Organic Thin-Film Solar Cells
（数理モデルによる有機薄膜太陽電池のモルフォロジーと性能に関する研究）

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Organic thin-film solar cells, OTFSCs, are promising energy harvesting devices because of their light weight, flexibility, low cost, suitability for roll-to-roll mass production, and short energy pay-back time. However, power conversion efficiencies, PCEs, of single junction OTSFCs are 11 % at highest, lower than silicon solar cells (~20 %), and optimization scheme is required. Active layer of an OTFSC is composed of organic donor and acceptor, which are respectively a π-conjugated polymer, and a fullerene-derivative or a “non-fullerene” π-conjugated small molecule.

Material properties is important to enhance OTFSC performance, to which many studies have been devoted. It is however unrealistic to experimentally examine all the combinations of the material properties. The morphology of OTFSC—the degree of phase separation, miscibility, and crystallinity of the organic semiconducting materials—is also significant for performance improvement since it strongly affects exciton dissociation and charge collection via accessibility to interface and electrodes, respectively. Bulk heterojunction, BHJ, is a breakthrough of OTFSC development. Morphology depends on such manufacturing conditions as drying rate, and annealing temperature and duration. Thermal annealing is widely performed to improve performance, and existence of optimal temperature is well known: annealing grows domains and increases crystallinity, leading to higher absorption and charge mobility, while excessive domain separation decreases efficiencies at temperature above the optimum. A problem is that (i) it is difficult to obtain high-resolution three-dimensional information on morphologies, and that (ii) combination of materials and other conditions like donor–acceptor ratio affects the optimum temperature, which requires experimental try-and-error. On the other hand, theorist have generated morphologies by means of molecular dynamics, Ising model, Cahn–Hilliard equation, reptation, etc. Device-scale (~100 nm) morphologies are necessary for evaluation of performance.

However, morphologies were characterized by such parameters as bond orientational correlation function, interfacial area and domain width, which are non-injective, and unsuitable for efficient screening and descriptors of machine learning. It is suggested that entropy promotes charge separation, which has not been examined in terms of morphology-dependence and effects on performance.

It is eventually challenging to test the combinations of material properties and morphologies exhaustively by experiments; theoretical works like dynamic Monte Carlo have been carried out to evaluate performances of OTFSCs, but few combinations of material properties and morphologies were examined. Therefore a new scheme is required.

The objective of this thesis is (i) to establish numerical characterization methods of morphologies; (ii) to reveal relationships between manufacturing conditions, morphologies, and performance; and finally (iii) to show material design guidelines.

This thesis is composed of five chapters: chapter 1 is devoted to general introduction and the objective described above.

In chapter 2, theoretical backgrounds are presented. Soft matter physics is explained to model polymer systems, and electrostatics to obtain analytical solution of potentials in active layers. Edit distance and graph algorithm are introduced for numerical evaluation of morphologies, and randomized algorithm and Monte Carlo method are explained.

In chapter 3, generation and numerical characterizations of morphologies are studied. Bulk hetero-junction morphologies (~100^3 nm^3) were generated by reptation, and Ising model for comparison. Tube model is a coarsened model of condensed polymer systems—polymer movement is restricted due to entanglement, and a polymer is enclosed in a tube; reptation is the thermal motion of polymer along "tube." The simulator was implemented to examine temperature-dependence of morphology by Metropolis Monte Carlo of reptation. In each Monte Carlo step energy change by trial reptation ΔE was calculated by the change in the coordination numbers Δn, and the interaction difference $\Delta\varepsilon := \varepsilon_{pp} - 2\varepsilon_{ps} + \varepsilon_{ss}$, where the subscripts p and s denote polymer and small molecule, respectively; negative $\Delta\varepsilon$ corresponds to mutually attractive polymers. The trial was accepted in probability of $\max\{1, \exp(-\beta\Delta E)\}$ with inverse temperature β. The effects of thermal annealing were considered by the dimensionless parameter $\beta\Delta\varepsilon$ in the simulations.

The generated morphologies were evaluated by such parameters as interfacial area and domain widths; the program based on graph algorithm was also implemented for further anal-

yses. Each lattice in a morphology was represented by the corresponding vertices, and the first nearest neighboring vertices were connected by edges. Breadth first search, BFS, was performed to divide a graph into disconnected subgraphs, *i.e.* isolated donor and acceptor domains; volume and interfacial area of each domain was calculated. Entropy and Helmholtz energy of charge separation was also evaluated. For each pair of donor–acceptor domain, density of states, DOS, was calculated as the number of the possible configurations of a hole and an electron in the corresponding domains, as a function of electron–hole distance; then entropy and Helmholtz energy were calculated. The pairs of donor–acceptor domains were restricted to those contiguous to examine entropy and Helmholtz energy of electron–hole pairs generated by exciton dissociation on interface.

Morphologies generated by reptation are shown in Figure 1. Domain growth under thermal annealing was reproduced. The interfacial area indicated the minimum value around $\beta\Delta\varepsilon = -1$ because of the degree of diffusion. At low temperature, *i.e.* low $\beta\Delta\varepsilon$, polymers are hindered in diffusing and trapped in a local minimum. At higher temperature, the polymers become able to diffuse and relax, leading to formation of domains; free diffusion, however, breaks the domains when the temperature is too high ($\beta\Delta\varepsilon \rightarrow -0$). BFS revealed that each BHJ morphology has a single gigantic donor domain, and a gigantic and many small acceptor domains. DOS increased between linearly and quadratically, whose extents depends on donor–acceptor pairs. It was revealed that Helmholtz energies were drastically decreased by entropies, and took the maximum values around electron–hole distance of 6 nm and then mildly decreased. A barrier—energy required to overcome the maximum—of gigantic acceptor domain is lower than those of small domains, and morphologies with smaller interfacial area tends to have lower barrier. This is because smooth interface of such morphologies makes DOS and entropy increase rapidly. It is

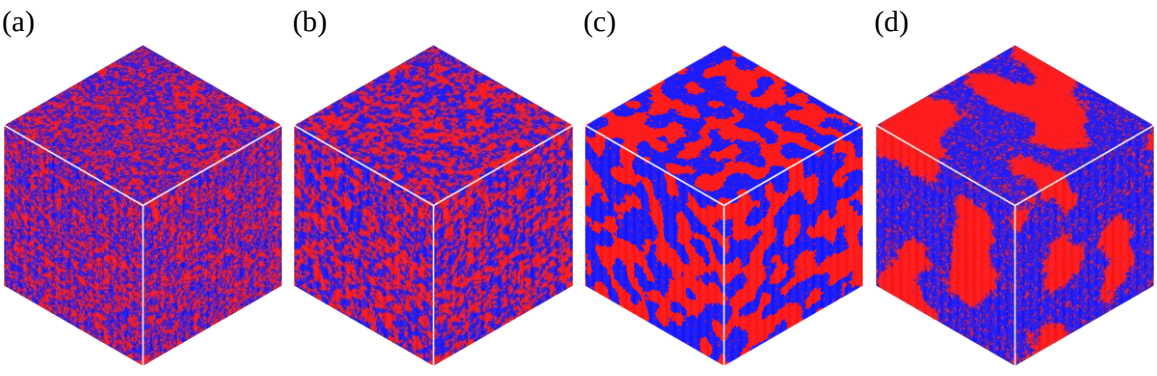

Figure 1: (a) An initial morphology—polymers were randomly configured; morphologies generated by reptation with $\beta\Delta\varepsilon$ of (b) −4, (c) −1, and (d) −0.5. The blue and red lattices represent polymers (donor) and small molecules (acceptor), respectively. Reprinted from *Phys. Chem. Chem. Phys.*, 2016, **18**, 26456–26465 under CC BY 3.0 license.

suggested that barrier is controllable by annealing temperature.

In chapter 4, performances of organic thin-film solar cells are studied by Dynamic Monte Carlo, DMC, simulations. Elementary processes in photoelectric conversion, *e.g.*, exciton generation and charge hopping, were mathematically modeled. The simulation procedure is as follows: (i) initialize the system; (ii) for each possible event, calculate waiting time by its rate and a random number; (iii) execute the event with the shortest waiting time, which is added to the elapsed time; (iv) repeat (ii)–(iii). Photo-and dark current density, transient absorption spectroscopy, and conductive atomic force micro were simulated by considering the corresponding events. Separation efficiencies at interfaces were also evaluated by simulation of a hole and an electron. The DMC simulator and the backends were implemented to treat the combinations of over a dozen properties morphologies, which is applicable to high-throughput screening and generation of dataset for machine learning.

Photo- and dark-current density–voltage characteristics depended on morphologies: morphology-dependence of short-circuit current density is due to trade-off between exciton dissociation and charge collection; morphology-dependence of open-circuit voltage is due to balance of photo- and dark current. Therefore, power conversion efficiencies depend on morphologies and take the maximum at $\beta\Delta\varepsilon = -1$, which agrees with experiments. Simulations of transient absorption spectroscopy revealed that the excitons generated on interfaces immediately (~1 ps) dissociate into holes and electrons, which is dominant, while the remaining excitons later (~100 ns) migrates to interface and dissociate, or recombine. This tendency is noticeable in morphologies with greater interfacial area and smaller domain widths, generated under lower temperature, *i.e.* lower $\beta\Delta\varepsilon$. On the other hand, such morphologies more rapid decay of charge carriers due to the trade-off. These observations agree with experimental results. C-AFM simulations agreed with experimental results, which will offer three-dimensional information on morphologies from experiments by high-throughput computation.

The DMC simulator also revealed that interface of large donor domain–large acceptor domain tends to have higher separation efficiencies than those of large donor domain–small acceptor domains, namely the latter is recombination centers. Comparison between morphologies revealed entropic effect on performance: morphologies with lower barriers show higher separation efficiencies. This suggests that acceptors that hardly separate is favorable for OTFSCs.

In chapter 5, general conclusion and future outlook are presented. These computational analyses can provide design guidelines to improve performances of OTFSCs.