

Monte Carlo Simulations of Crystalline Organic Semiconductors

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Abstract: Molecular model for crystalline organic semiconductors based on small molecules is implemented in three-dimensional Monte Carlo simulations. In this paper results for naphthalene are presented. Molecular structure is considered in two configurations: within a single monocrystal and in vicinity of interface between two monocrystals with different crystalline orientations.

Keywords: Organic semiconductors, Monte Carlo algorithm, Polycrystal.

1 Introduction

Idea of using organic materials as active elements for electronic devices was proposed only a few years after the first classical silicon-based electronic device had been made [1 – 3]. Research on organic semiconductors has been intensified during 90s for two reasons: (1) experiments proved that it was possible to make organic lights emitting diodes (OLED) [1, 4 – 7], organic thin film transistors (OTFT) [1, 8] and organic solar cells (OPV) [1, 9]; (2) at the same time new cheap semiconducting devices were required. At this moment, organic LEDs are on the market, but OTFTs and OPVs are still subject of research effort, which includes development of new materials, processing techniques and devices architectures [1].

Organic semiconductors can be either polymer or based on small molecules. The organic semiconductors with small molecules exist both in amorphous and crystalline state. Small molecules used in the organic semiconductors are frequently aromatic hydrocarbons such as naphthalene, anthracene, pentacene, rubrene etc. PPV, P3HT are examples of polymer semiconductors. In this paper simulations of naphthalene are presented.

Organic thin film based on the naphthalene crystal is typically polycrystalline, which means that inside one polycrystalline film there are many contact interfaces (grain boundaries) between different monocrystals with different crystalline orientations. Grain boundaries are believed to be a

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bottleneck for charge carrier transport in organic semiconductors. Exact physics of the transport at grain boundaries is still not known.

The goal of this work is modeling of the structure of a grain boundary between two naphthalene monocrystals with a given angle of disorientation. For this purpose, simulations based on well-known classical Monte Carlo (MC) method were developed. Until now, Monte Carlo method has been widely used for quantum mechanical simulations of organic semiconductors, mostly for charge transport modeling. Yao and co-workers have applied MC method to determine waiting time and diffusion coefficient of carriers in pentacene [10]. Further, Monte Carlo-based transport simulator has been developed to calculate field and temperature dependent mobility in thiophene- and porphyrin-based OTFTs [11]. Dynamical MC has been used to obtain the dependence of internal quantum efficiency of an organic bulk heterojunction PFB/F8BT solar cell [12]. In this paper, classical molecular MC is used for the first time to investigate the role of grain boundaries in naphthalene. In Section 2 the methodology is described, while results of the simulation of a bulk naphthalene monocrystal and the structure around the grain boundary of two monocrystals are presented in Section 3.

2 Method Description

The crystal structure of naphthalene is illustrated in Fig. 1. The unit cell of naphthalene crystal is monoclinic [10] (two pairs of unit vectors are perpendicular) and contains 2 molecules with angle between them of 51.9° . The Lennard-Jones potential is used to describe interaction between molecules and the Monte Carlo method to obtain the structure at finite temperature.

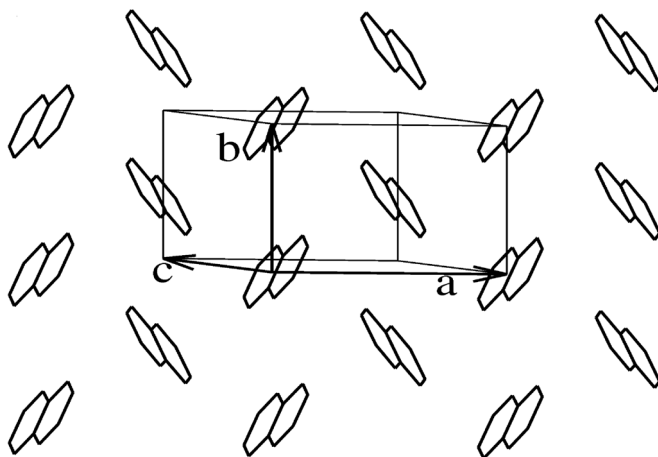


Fig. 1 – The crystal structure of naphthalene. Dimensions of the unit cell are: $a = 0.824$ nm, $b = 0.6$ nm and $c = 0.866$ nm [10].

2.1 Lennard – Jones Potential

Interaction between molecules is described using Lennard – Jones potential, which is given by formula:

$$v^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is a distance between CH groups from different molecules. When calculating the total energy of the simulated system, only interactions of CH groups from different molecules are considered. The shape of the potential is illustrated in Fig. 2.

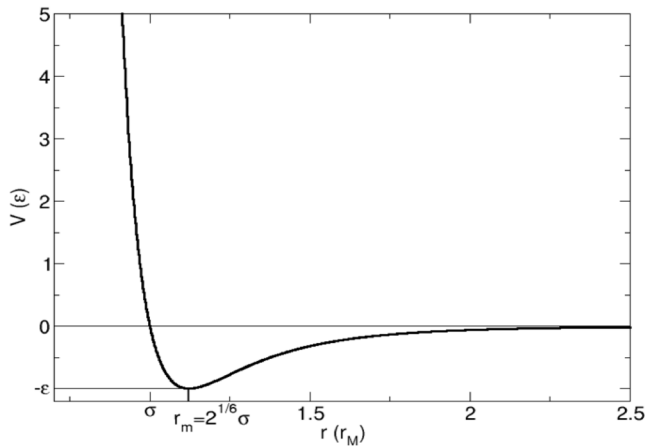


Fig. 2 – Lennard Jones Potential.

Here, ϵ is absolute value of potential at the minimum and it is called potential depth. Parameter σ is distance between atom groups at which the interaction potential is 0. As we can see in Fig. 2, potential for distances greater than 2σ is very small compared to molecule kinetic energy at the room temperature. Here, it is convenient to introduce cut-off parameter for the potential at 4σ . In such a way, simulation becomes faster without lower certainty of the results. In our simulations, scaled Lennard Jones Potential is used ($\epsilon = \sigma = 1$). Therefore all variables should be scaled using scaled units: (1) distance $d^* = \sigma = 0.37\text{nm}$, (2) density $\rho^* = 1/\sigma^3 = 20\text{ nm}^{-3}$ and (3) temperature $T^* = \epsilon/k_B = 50\text{ K}$ [14, 15].

2.2 Monte Carlo Method

Monte Carlo Algorithm is schematically described in Fig. 3. Molecules are considered as rigid and in-plane, therefore their shape and bonding lengths between atoms are constant during the simulation. The center of mass of a molecule has 6 degrees of freedom: 3 translational and 3 angles which describe

rotation. We use Tait-Bryan angles, which represent one of the Euler angles conventions. The algorithm starts from a given or a random configuration of molecules [16]. Two types of predefined configurations are possible: (1) monocrystalline and (2) interface. In the case of interface, the initial configuration is created from two monocrystals joined together with a defined angle between them. After an initial configuration is created, two nested cycles start. The first cycle is repeated M times, where M is given number of MC steps, and the second is repeated N times, where N is number of molecules in the system. In each MC step the energy of the system E_{int} is calculated. Then, one molecule is randomly chosen, translated and rotated. In total, during the MC simulations maximal $N \times M$ random moves of randomly chosen molecules are tried. After each change of the configuration, energy of the new configuration of E_{new} is calculated. The change is accepted or not according to the Metropolis condition: if new energy is lower than the initial, new configuration is accepted, if it is not, than it is accepted with a probability equal to the Boltzmann weight of the difference of the new and the initial energy, i.e., $\exp[-(E_{\text{new}} - E_{\text{init}})/k_B T]$ see [16, 17]. The Monte Carlo simulation reaches thermal equilibrium when the total potential energy of the system start to oscillate around a fixed value. An evolution of the total potential energy during MC run is shown in Fig. 4 for a typical simulation performed at 300 K. The obtained configuration is afterwards cooled down to 0 K, also using MC simulation. The cooling rate is chosen so that the equilibrium crystal structure is recovered.

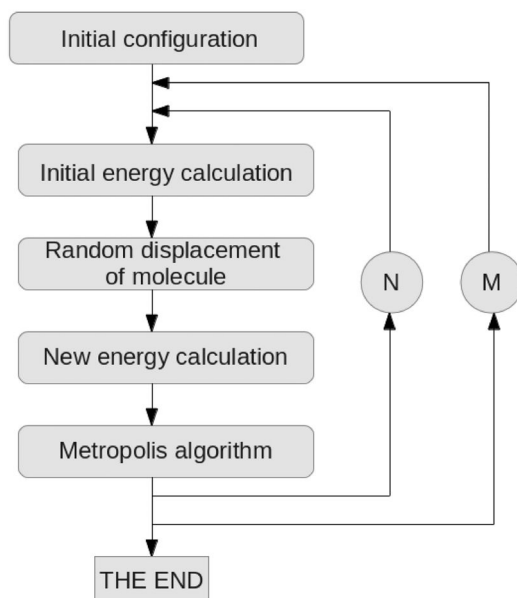


Fig. 3 – *The Monte Carlo algorithm.*

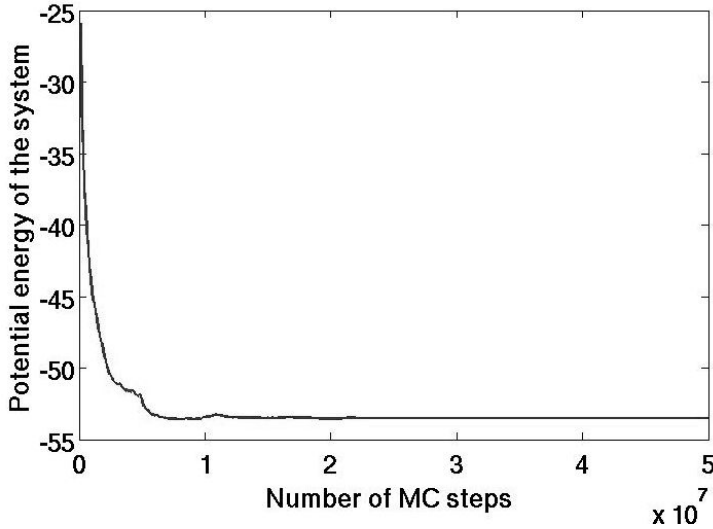


Fig. 4 – Evolution of the potential energy of the system with $N = 1000$ naphthalene molecules.

2.3 Order parameter

In order to monitor level of the orientational order in the obtained structure we use the order parameter [18]. The order parameter is defined by the vector, called director, which is directed through the reference axis of a molecule. Orientation of the molecule is described by two angles φ and θ . The components of director are given by equations:

$$\vec{u}_x = \cos \varphi \sin \theta, \quad (2)$$

$$\vec{u}_y = \sin \varphi \sin \theta, \quad (3)$$

$$\vec{u}_z = \cos \theta. \quad (4)$$

Using this components the matrix is formed:

$$Q_{\alpha\beta} = \frac{1}{2N} \sum_i (\vec{u}_{\alpha i} \vec{u}_{\beta i} - \delta_{\alpha\beta}), \quad (5)$$

where is N number of molecules, α and β are combination of x , y , z axes and $\delta_{\alpha\beta}$ is the Kronicker function [18]. Diagonalization of the matrix gives 3 eigenvalues. Maximal eigenvalue is the order parameter. It has values from 0 to 1. Crystal structure has the order parameter close to 1, liquid crystal between 0.1 and 0.4 and isotropic system under 0.1 [18].

3 Results

3.1 Simulations of naphthalene monocrystal

For the algorithm correctness checkout, the naphthalene bulk monocrystal is simulated. During the simulation, number of molecules, temperature and volume are kept constant (NVT ensemble). System consists of 1000 molecules arranged in 10 layers parallel to the *ab* plane. In Fig. 5, the potential energy and the order parameter dependence on temperature are given. Temperature rises from 0 K to the just below melting temperature of 350 K. The potential energy increases and the order parameter decreases with the temperature increase. Still, since the material maintains its crystal structure both magnitudes of the potential energy (compared to molecular kinetic energy) and order parameter remain high.

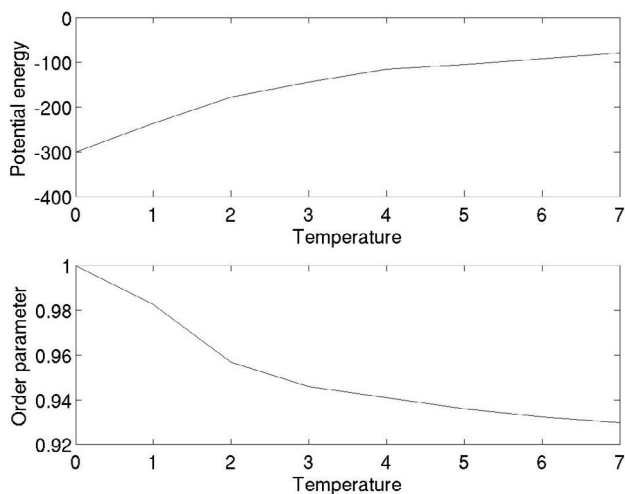


Fig. 5 – a) Potential energy dependence and
b) order parameter dependence on temperature.

All variables are expressed in non-dimensional Lennard-Jones units.

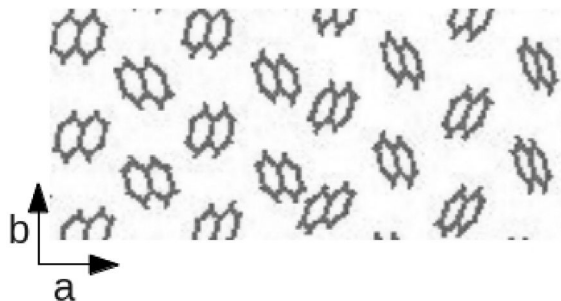


Fig. 6a – The molecular structure over naphthalene polycrystal for angle between monocrystal of 5° .

All variables are expressed in non – dimensional Lennard Jones units.

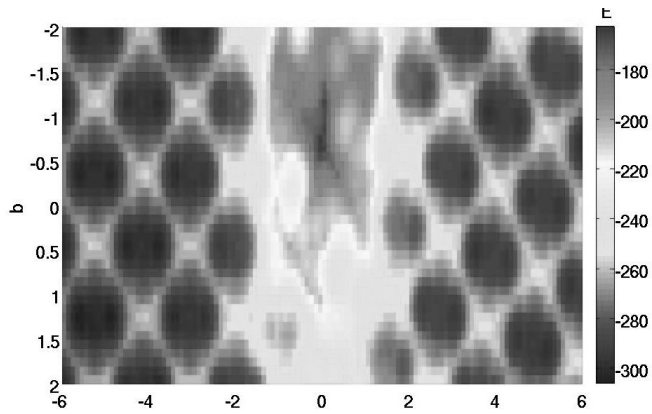
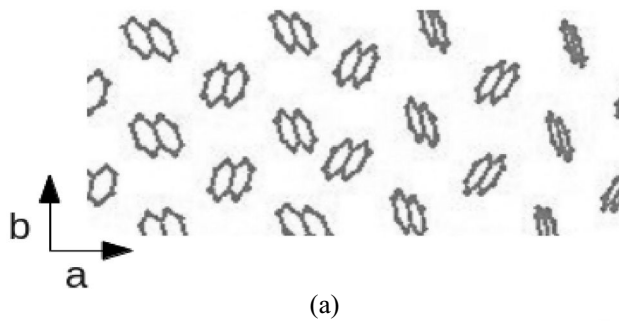
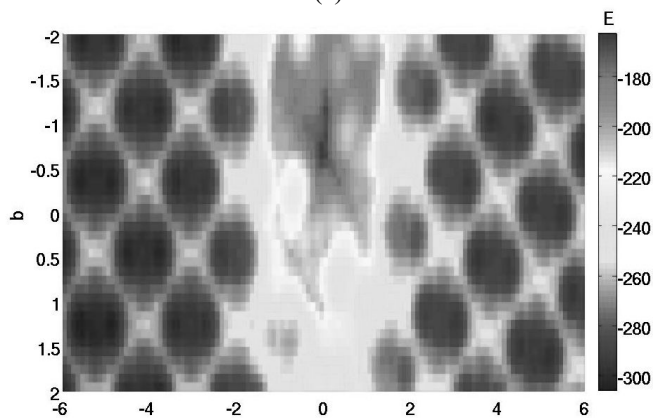


Fig. 6b – Energy distribution over naphthalene polycrystal for angle between monocrystal of 5° . All variables are expressed in non – dimensional Lennard Jones units.



(a)



(b)

Fig. 7 – The molecular structure (a) and energy distribution (b) over naphthalene polycrystal for angle between monocrystal of 10° . All variables are expressed in non – dimensional Lennard Jones units.

3.2 Simulations of grain boundaries between two monocrystals

In this section, results of simulations of grain boundaries in naphthalene polycrystal are presented. The interface is created by joining two monocrystals with different crystalline orientations. The number of molecules is 500 in each monocrystal. The grain boundary is perpendicular to a direction of the unit cell of the naphthalene crystal. Our results indicate that the molecular structure of the monocrystal grains is changed only in the vicinity of the grain boundary. Fig. 6 and Fig. 7 show the molecular structure of grain boundaries as well as the energy distribution over one ab plane for angles between monocrystals of 5° and 10° . The highest energies are concentrated on the grain boundary. In Fig. 8 potential energy dependence on the angle between monocrystals is given. The energy increases as angle increases.

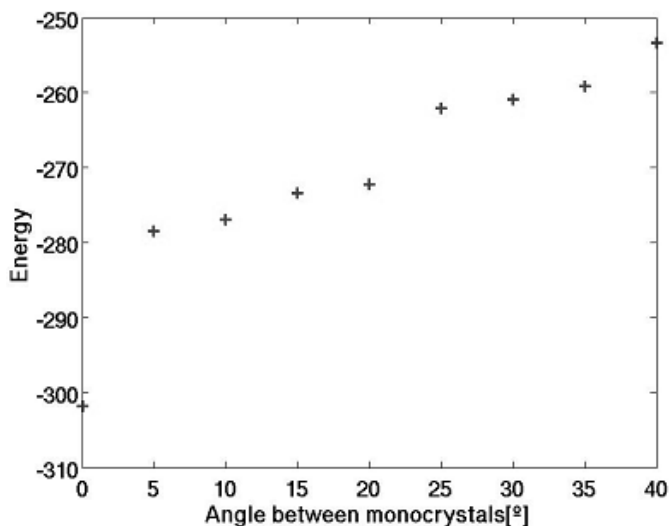


Fig. 8 – The potential energy of a polycrystal dependence on angle between monocrystals. Energy is expressed in non – dimensional Lennard Jones units.

4 Conclusion

In this paper, three-dimensional Monte Carlo simulations are presented, in which the molecular model for crystalline organic semiconductors based on the naphthalene is implemented. The dependence of potential energy and order parameter on temperature in the crystalline naphthalene are evaluated. The results for the bulk naphthalene monocrystal and for the grain boundaries in the naphthalene polycrystal are shown. The results for naphthalene polycrystal

indicate that grain boundaries have impact on the molecular structure of the polycrystal only in the nearest environment of the boundaries. Molecules near the boundary have significantly higher energies than molecules far from the boundary. Also, their orientation is different from the orientation of molecules in monocrystal grains. Obtained results for the molecular structure of grain boundaries in naphthalene polycrystals will be used for electronic calculations which should give answer how do grain boundaries affect transport properties of crystalline organic semiconductors based on small molecules.

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6 References

- [1] D.L. Cheung, A.Troisi: Modelling Charge Transport in Organic Semiconductors: From Quantum Dynamics to Soft Matter, *Physical Chemistry Chemical Physics*, Vol. 10, No. 39, Aug. 2008, pp. 5941 – 5952.
- [2] M. Berggen, D. Nilsson, N.D. Robinson: Organic Materials for Printed Electronics, *Nature Materials*, Vol. 6, No. 1, Jan. 2007, pp. 3 – 5.
- [3] S. R. Forrest: The Path to Ubiquitous and Low-cost Organic Electronic Appliances on Plastic, *Nature*, Vol. 428, No. 6986, April 2004, pp. 911 – 918.
- [4] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A.D. Santos, J.L. Bredas, M. Logdlund, W.R. Salaneck: Electroluminescence in Conjugated Polymers, *Nature*, Vol. 397, No. 6715, Jan. 1999, pp. 121 – 128.
- [5] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holms: Light-emitting Diodes based on Conjugated Polymers, *Nature*, Vol. 347, No. 6293, Oct. 1990, 347, pp. 539 – 541.
- [6] V.L. Colvin, M.C. Schlamp, A.P. Alivisatos: Light-emitting Diodes Made from Cadmium Selenide Nanocrystals and a Semiconducting Polymer, *Nature*, Vol. 370, No. 6488, Aug. 1994, pp. 354 – 357.
- [7] W.L. Kalb, S. Haas, C. Krellner, T. Mathis, B. Batlogg: Trap Density of States in Small-molecule Organic Semiconductors: A Quantitative Comparison of Thin-film Transistors

- with Single Crystals, *Physical Review B: Condensed Matter and Materials Physics*, Vol. 81, No. 15, April 2010, p. 155315.
- [8] G. Li, V. Shrotriya, J.S. Huang, Y. Yao, T. Morairty, K. Emery, Y. Yang: High-efficiency Solution Processable Polymer Photovoltaic Cells by Self-organization of Polymer Blends, *Nature Materials*, Vol. 4, No. 11, Nov. 2005, pp. 864 – 868.
- [9] A. Dodabalapur, L. Trosi, H. E. Katz: Organic Transistors: Two-dimensional Transport and Improved Electrical Characteristics, *Science*, Vol. 268, No. 5208, April 1995, pp. 270 – 271.
- [10] M. Grundndmann: *The Physics of Semiconductors: An Introduction Including Nanophysics and Applications*, Springer, Berlin, Germany, 2010.
- [11] Y. Yao, W. Si, X. Hou, C. Q. Wu: Monte Carlo Ssimulation based on Dynamic Disorder Model in Organic Semiconductors: From Coherent to Incoherent Transport, *Journal of Chemical Physics*, Vol. 136, No. 23, June 2012, p. 234106.
- [12] A. Bolognesi, A. Di Carlo, P. Lugli, G. Conte: Large Drift-diffusion and Monte Carlo Modeling of Organic Semiconductor Devices, *Synthetic Metals*, Vol. 138, No. 1-2, June 2003, pp. 95 – 100.
- [13] P.K. Watkins, A.B. Walker, G.L.B. Verschoor: Dynamical Monte Carlo Modelling of Organic Solar Cells: The Dependence of Internal Quantum Efficiency on Morphology, *Nano Letters*, Vol. 5, No. 9, Aug. 2005, pp. 1814 – 1818.
- [14] C.D. Wick, M.G. Martin, J.I. Siepmann: Transferable Potentials for Phase Equilibria. 4. United-Atom Description of Linear and Branched Alkenes and Alkylbenzenes, *The Journal of Physical Chemistry B*, Vol. 104, No. 33, Aug. 2000, pp. 8008 – 8016.
- [15] M.G. Martin, J.I. Siepmann: Transferable Potentials for Phase Equilibria. 1. United-atom Description of n-Alkanes, *The Journal of Physical Chemistry B*, Vol. 102, No. 14, April 1998, pp. 2569 – 2577.
- [16] M.P. Allen, D.J. Tildesey: *Computer Simulations of Liquids*, Oxford University Press, NY, USA, 1999.
- [17] D. Frenkel, B. Smit: *Understanding Molecular Simulations: From Algorithms to Applications*, Academic Press, San Diego, CA, USA, 2002.
- [18] H. Steuer: *Thermodynamical Properties of a Model Liquid Crystal*, PhD Thesis, Technical University Berlin, Berlin, Germany, 2004.