Monte Carlo studies of polymer aggregation

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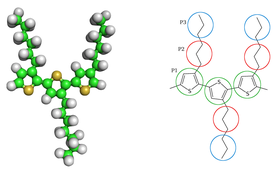
Introduction

Poly(3-hexylthiophene) (P3HT) is a semiconducting polymer that has applications in organic photovoltaics. It is widely used as a semi-conducting layer in organic solar cells.
We found that a recently developed coarse-grained model of P3HT, is suitable and able to reproduce not only fully atomistic simulations, but also experimental results. On the basis of those single-chain studies, we now take the next step and look at aggregation of a few polymers, to gain an understanding of the fundamental processes that happen during the crystallization of P3HT. With parallel tempering simulations we investigate a system of four P3HT polymer chains with 10 repeat units each in the presence of a Au(001) surface and without a substrate.
In addition to that, we aim to apply the parallel multicanonical (PMUCA) sampling method to our system. A recent implementation of PMUCA on GPUs, promises vast increase in efficiency of the multicanonical weight recursion and production run. An early implementation for polymer aggregation using this novel approach is presented here.

P3HT coarse-grained model[1]



Atomistic (left) and coarse-grained (right) representation of a 3-mer of hexylthiophene.

$$U_{\text{bond}}(l) = \sum_{i=2}^{n} a_i (l - l_0)^i$$

$$U_{\text{bending}}(\Theta) = \sum_{i=0}^{n} b_i (\Theta - \Theta_0)^i$$

$$U_{\text{torsion}}(\Phi) = \sum_{i=0}^{n} c_i \cos^i(\Phi)$$

$$U_{\text{improper}}(\xi) = \sum_{i=1}^{5} (-1)^{n+1} d_i \xi^{2n}$$

One repeat unit of the polymer is represented by three coarse-grained (CG) particles (P1, P2 and P3).

P1 includes the thiophene ring.
P2 and P3 each include 3 carbons with the corresponding hydrogens of the hexyl-sidechain.

CG model uses around 100 parameters.

In addition to the given potentials the model includes non-bonded potentials, which include Lennard-Jones and Coulomb interactions.

Studies of single chains isolated and in presence of a Au(001) surface can be found in [2-4].

[1] D.M. Huang, R. Faller, K. Do, A.J. Moule, J. Chem. Theory Comput. **6**, 526 (2010).

[2] S. Förster, E. Kohl, M. Ivanov, J. Gross, W. Widdra, W. Janke, J. Chem. Phys. **141**, 164701 (2014).

[3] J. Gross, M. Ivanov, W. Janke, J. Phys.: Conf. Ser. **750**, 012009 (2016).

[4] M. Ivanov, J. Gross, W. Janke, Eur. Phys. J. – Spec. Top. **226**, 667 (2017).

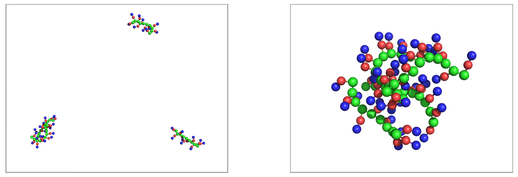
Simulation and results

Replica-exchange (parallel tempering) simulations with 12 temperatures in the range of 200K–550K.

Simulation of four polymers with 10 repeat units each.

Box with fixed boundaries of size (350Å x 350Å x 100Å).

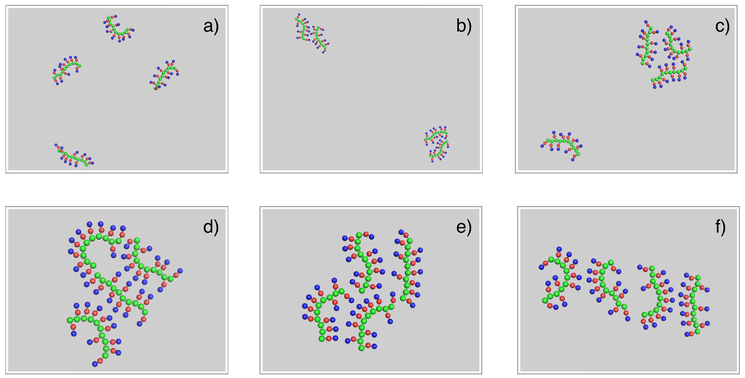
without surface



Separated polymers at high temperatures (550K) on the left. Aggregated polymers in a globule conformation at low temperatures (200K) right.

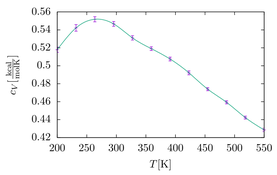
In the simulated temperature range the polymers in the box are in an aggregate at almost all temperatures.
The aggregation transition happens around or above 550K.

with Au(001) surface



Aggregation stages of four P3HT polymers with 10 repeat units each adsorbed on a Au(001) surface. Conformations a)–c) are found at high temperatures where the polymers are moving separately on the surface. Aggregated conformations d)–f) are found at low temperatures.

The specific heat curve shows a peak at around 270K suggesting the aggregation temperature. This is confirmed by the conformations found above and below that temperature.

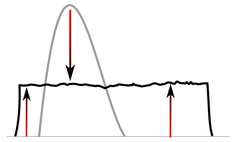


Parallel multicanonical simulations on GPUs

The canonical partition sum can be written as a function of the density of states $\Omega(E)$

$$\mathcal{Z}_{\text{can}} = \sum_E \Omega(E) e^{-\beta E} \rightarrow$$

$$\mathcal{Z}_{\text{muca}} = \sum_E \Omega(E) W(E)$$

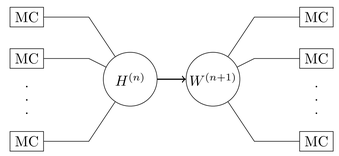


For a flat histogram $W(E) \propto \Omega^{-1}(E)$

We have to estimate the density of states through an iterative process:

$$W^{(n+1)}(E) = \frac{W^{(n)}(E)}{H^{(n)}(E)}$$

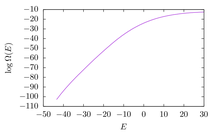
The computationally expensive process of generating the weights can be done in parallel [5]. Communication happens only once per iteration to merge the histograms and distribute the new weights.



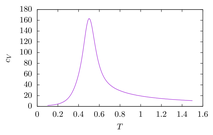
This parallel multicanonical method can very efficiently be used on general purpose graphics processing units (GPGPUs) [6].

A GPU implementation applied to the simulation of a simple coarse-grained, flexible polymer in 2D is the first step to enabling this advanced method for more complex simulations with P3HT. Results from these simulations are shown here.

With this method the density of states can be determined over several orders of magnitude. Through reweighting techniques canonical observables can obtained.



Density of states for a system of four polymers with 10 monomers each.



The specific heat shows a pronounced peak signaling the aggregation.

Two exemplary conformations of a system of four polymers with 10 monomers. Aggregate at low temperatures (left). Separated conformation at high temperatures (right).

[5] J. Zierenberg, M. Marenz, W. Janke, Comput. Phys. Commun. **184**, 1155 (2013).

[6] J. Gross, J. Zierenberg, M. Weigel, W. Janke, to appear in Comput. Phys. Commun. (2017).

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