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Comparing atomistic and coarse–grained simulations of P3HT

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Abstract. Poly(3–hexylthiophene) (P3HT) is a key material used in organic photovoltaics. In this study we assess the validity of two coarse–grained models of P3HT by comparing coarse–grained Monte Carlo simulations to fully atomistic molecular dynamics simulations. Structural properties of single polymer chains of short to medium lengths are compared between the three representations.

1. Introduction

The interest in Poly(3–hexylthiophene) (P3HT) comes from its application in organic photovoltaics due to its electronic and optical properties [1, 2]. For a better understanding of the polymer in interaction with other materials several experimental and theoretical studies have been published in recent years [3, 4, 5, 6]. It is a very common simulational approach to use coarse–grained models to study a wide range of properties of a given system. With this strategy it is much faster to sample the phase space compared to an all–atom study, but this comes at the cost of losing some detail. In a previous work [7] we investigated the adsorption behavior of P3HT on reconstructed gold surfaces using experimental and simulational approaches (see Fig. 1 for exemplary structures). In the current work we compare two different types of coarse–grained models using Monte Carlo (MC) simulations with all–atom molecular dynamics (MD) simulations. We want to determine which one of the two coarse–grained models matches the all–atom simulations best.

Figure 1. Scanning tunneling microscopy image of a P3HT 50–mer on Au(001) (left) and elongated 50–mer conformation on a surface obtained by Monte Carlo simulations (right).

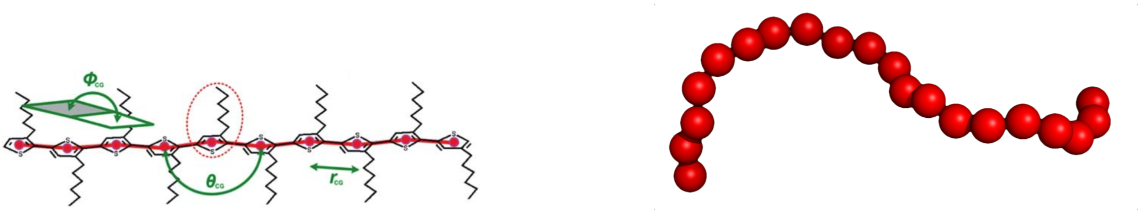

Figure 2. Schematic coarse–graining idea (after Ref. [3]) (left) and resulting homopolymer model (right).

2. Models

In this section we introduce the two coarse–grained (CG) models and the parameterization of the all–atom MD simulations. The first CG representation (Model A) we investigated in this work is a simple homopolymer model where every unit of P3HT has been coarse–grained into a single CG bead at the center of mass of the corresponding monomers of the atomistic chain. The interactions between the CG particles of Model A are given by a harmonic potential to model the bonds $U_{\mathsf{bond}}(l) = \frac{1}{2}k_b \cdot (l - l_0)^2$, a harmonic term for the bending energy $U_{\mathsf{bending}}(\Theta) = \frac{1}{2}k_\Theta \cdot (\Theta - \Theta_0)^2$, a dihedral angle potential of the following form $U_{\mathsf{torsion}}(\Phi) = \frac{1}{2}\sum_{n=1}^{3} V_n \left[1 + (-1)^{n-1}\cos(n\Phi)\right]$, and finally Lennard-Jones like interactions for all non–bonded particles $U_{\mathsf{non\text{-}bonded}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$. To obtain the 9 parameters for these potentials, atomistic MD simulations have been run and the iterative Boltzmann inversion method [8, 9] was applied. For details and the actual parameters please refer to [3]. This model was originally developed to describe the interaction of P3HT with a fullerene derivate phenyl-C_{61}-butyric acid methyl ester (PCBM) in melts as they occur in aforementioned solar cells. A schematic representation of the coarse–graining ansatz and the resulting homopolymer bead–spring model are depicted in Fig. 2.

The second representation (Model B) allows for some more detail since it includes information on the side–chains (see Fig. 3 on the left). Here we distinguish three coarse–grained particles. P1 are the backbone particles with their origin in the center of mass of the thiophene ring. The side–chains in this CG model are represented by two beads P2 and P3, each including three methyl groups. A sketch of the structure can be found in Fig. 3 on the right. As with Model A the parameters of the CG potentials for this model were determined by MD simulations and calculated using the iterative Boltzmann inversion method [4]. The resulting potential for the bonds between particles $U_{\mathsf{bond}}(l) = \sum_{i=2}^{n_b} c_i \,(l - l_0)^i$, has a total of 26 parameters for the three

Figure 3. Atomistic structure of a P3HT 3–mer in bead-stick representation (left) and a sketch of the three beads per monomer coarse–grained Model B (right).

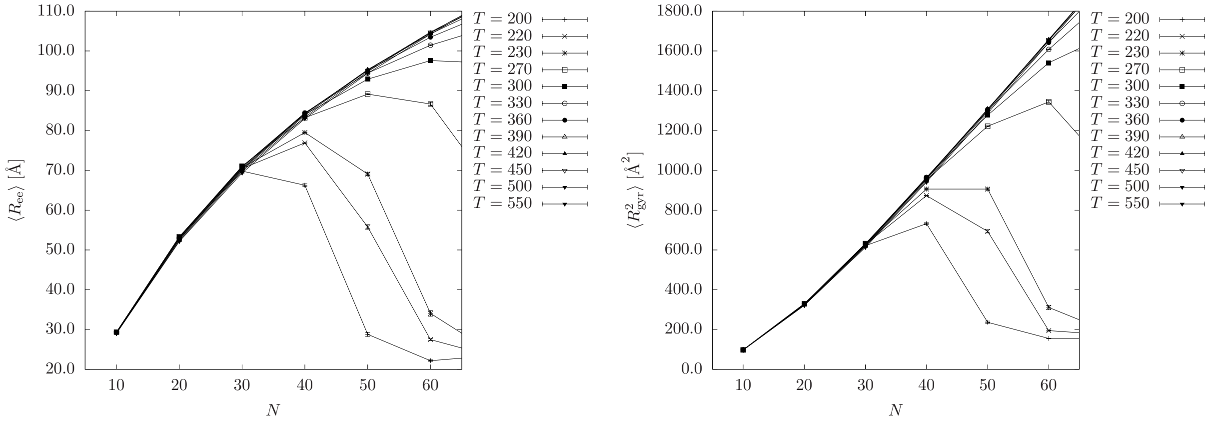

Figure 4. Model A: End–to–end distance (left) and squared radius of gyration (right) for lengths $N = 10$ to 60 at temperatures in the range from $T = 200\,\mathrm{K}$ to $550\,\mathrm{K}$.

types of possible bonds (P1-P1, P1-P2, and P2-P3). Angles between two bonds contribute to the total energy via $U_{\mathsf{bending}}(\Theta) = \sum_{i=0}^{n_a} c_i \left(\Theta - \Theta_0\right)^i$, with a total of 42 parameters. The dihedral interaction is described by $U_{\mathsf{torsion}}(\Phi) = \sum_{i=0}^{n_t} \cos^i(\Phi)$ with 24 parameters. Finally, the last potential to model bonded interactions is a polynomial with 5 parameters describing the improper dihedral for P1-P2-P1-P1. Additionally, the original paper for this model includes 4 pages of tabulated values which describe the non–bonded interaction, which include Lennard–Jones and Coulomb interactions. This leads to a total number of 97 parameters for this coarse–grained model, not counting the non–bonded table. It is rather unusual to have such a large number of parameters, since the idea of coarse-graining is the reduction of degrees of freedom.

To simulate the atomistic model we employ the all–atom variant of the Optimized Potentials for Liquid Simulations (OPLS-AA). This force field contains four contributions, the bonds using $U_{\mathsf{bond}}(r) = \frac{1}{2} k_b \left(r - r_0\right)^2$, the angles with $U_{\mathsf{bending}}(\Theta) = \frac{1}{2} k_\Theta \left(\Theta - \Theta_0\right)^2$, the third contribution has two terms describing the proper and improper dihedrals, $U_{\mathsf{torsion}}(\Phi) = \sum_{i=0}^{5} k_i \cos\left(\Phi - \pi\right)$ and $U_{\mathsf{improper}}(\Phi) = k\left[1 + d\cos\left(n\Phi\right)\right]$, and lastly the non–bonded contribution, which includes Lennard-Jones and Coulomb interactions. An exemplary structure of a 3–mer is shown in Fig. 3 on the left.

3. Geometrical comparison

For models A and B we performed replica-exchange Monte Carlo simulations at 12 temperatures in the range from $T = 200\,\mathrm{K}$ to $550\,\mathrm{K}$ for different numbers of monomers N ranging from 10 to 60. The quantities we want to focus on in this study are two basic geometric properties that are also accessible in experiment and thus allow for comparison with our simulational results. Firstly we look at the end–to–end distance $R_{\mathrm{ee}} = |\vec{r}_N - \vec{r}_1|$ and secondly the squared radius of gyration $R^2_{\mathrm{gyr}} = R^2_{xx} + R^2_{yy} + R^2_{zz}$, with $R^2_{ij} = \frac{1}{N} \sum_{n=1}^{N} \left(r_i^{(n)} - \overline{r}_i\right)\left(r_j^{(n)} - \overline{r}_j\right)$ where N is the number of monomers, $r_i^{(n)}$ $(i = x, y, z)$ is the i-th Cartesian coordinate of the n-th monomer and $\overline{r}_i = \sum_{n=1}^{N} r_i^{(n)}/N$.

Figure 4 shows the end–to–end distance (left) and the squared radius of gyration (right) for Model A. Both quantities show the same behavior and allow for the same conclusions. All chains are elongated for temperatures above 270 K and chains that are longer that 30 monomers start collapsing at temperatures below 270 K. Noticeable is that at room temperature (300 K),

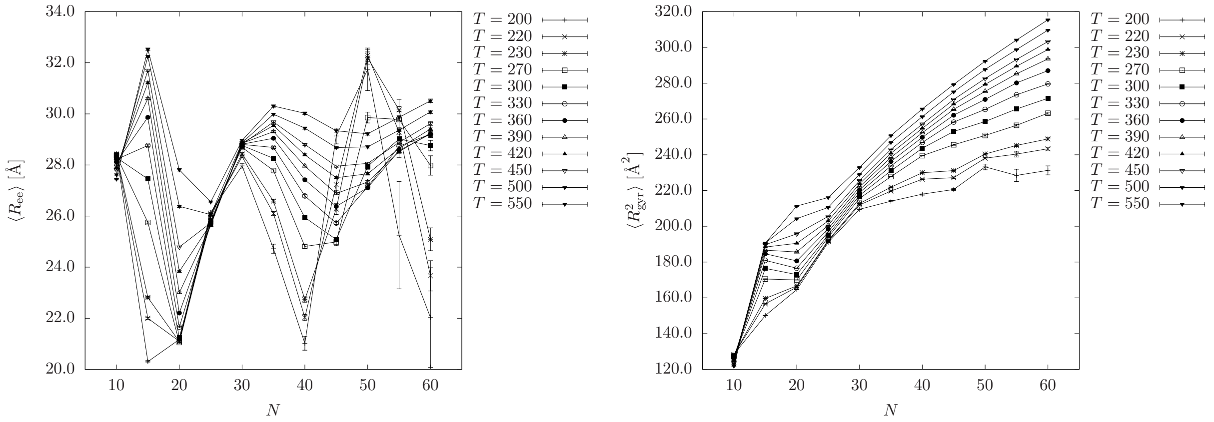

Figure 5. Model B: End–to–end distance (left) and squared radius of gyration (right) for lengths $N = 10$ to 60 at temperatures in the range from $T = 200\,$K to $550\,$K.

all chains are elongated. A fit to the radius of gyration data at that temperature results in a $R_{\rm gyr} \sim N^{0.74}$ scaling.

We show the same quantities for Model B in Fig. 5, but this time we see a completely different behavior. The end–to–end distance is almost the same for all chain lengths and rather short, suggesting a dense or collapsed structure. The temperature seems to have virtually no influence on the end–to–end distance. Also for the radius of gyration the temperature only plays a minor role. The values of the radius of gyration also suggest much more closely packed structures, when compared to those of Model A. We come to the conclusion that in this model the chains at all temperatures are in a globule state, which agrees with the scaling for the radius of gyration that we again measure at room temperature to be $R_{\rm gyr} \sim N^{0.24}$.

For the atomistic model we employed molecular dynamics simulations using the GROMACS software package. We used the Velocity-Verlet integrator in combination with the massive Andersen thermostat. We decided to use a stochastic thermostat, since we are only interested in structures at certain temperatures and can neglect dynamics at this point. Simulations were run at $T = 300\,$K using a time step of 1 fs, which is of the order of the bond fluctuations. For

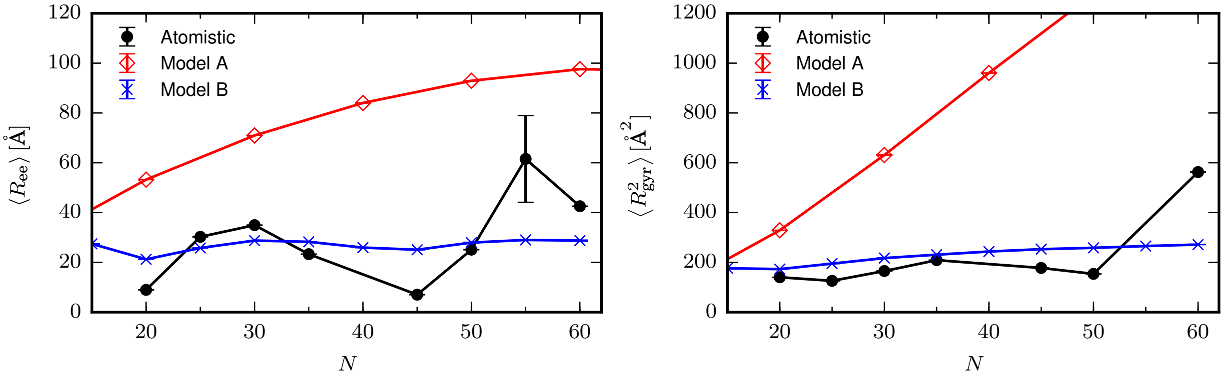

Figure 6. End-to-end distance (left) and squared radius of gyration (right) for the coarse–grained models A and B and the atomistic model at $T = 300\,$K. Errors for the atomistic model are of the order of the exemplary one shown for $N = 55$. For models A and B error bars are of the size of the symbols.

each chain length a trajectory of 100 ns was recorded. The results for the end–to–end distance and the squared radius of gyration are shown together with the respective results from Model A and B in Fig. 6. Even though the fluctuations in the MD results are quite large, especially for long chains, due to the slow convergence of MD simulations in general, the agreement of the results with those from Model B are indisputable. The polymer is in a globule state for all chain lengths at room temperature.

To examine the source of the difference in the result we look at the persistence length as a final quantity. The persistence length l_p is here defined as the length where the average $\cos\Theta(s)$ reaches the value $1/e$, with $l_b \approx 4\,\text{Å}$, $s = |i-j|$ and

$$\langle \cos\Theta(s)\rangle = \langle \vec{a_i}\cdot\vec{a_j}\rangle / \langle a_i^2\rangle = \exp(-s l_b/l_p), s\to\infty.$$

This is also the standard calculation provided by the GROMACS package. While Model A exhibits persistence lengths between 30 Å and 40 Å, Model B and the atomistic simulations agree on a persistence length of only approximately 15 Å. This leads us to the conclusion that the parameterization for Model A overestimates the stiffness of a single polymer and that Model B is able to reproduce the stiffness behavior more appropriately.

Finally, we want to comment on the computing time involved in the above simulations. The times we give here are in units of core hours, although the actual simulations are, of course, run in parallel. This helps to put the computational effort of the different approaches in perspective. For the one–particle bead–spring polymer (Model A) we ran parallel–tempering simulations at 12 temperatures for 15 chain lengths with 10^8 Monte Carlo sweeps each. The total run time was 7800 hours which is approximately 325 days. Simulations of Model B at 12 temperatures for 11 chain lengths with 10^7 sweeps each took about 2000 hours corresponding to about 83 days. The atomistic simulations of 100 ns trajectories for 9 chain lengths and only one temperature took about 11000 hours which equals to about 450 days.

4. Summary

Our simulations confirm the suitability of Model B to realistically reproduce geometrical observables of single isolated P3HT polymer chains when compared to all–atom molecular dynamics simulations. Since the original parameterization of Model A was to replicate the behavior of P3HT with fullerene in melts, we find it not suitable for our single polymer studies. The persistence length and thus the stiffness of the polymer is clearly overestimated in Model A. Furthermore our comparison proves the striking advantage of coarse–grained Monte Carlo simulations compared to MD simulations in terms of efficiency and statistics.

Acknowledgments

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