

SUBMITTED VERSION

David M. Huang, Adam J. Moule and Roland Faller
Characterization of polymer-fullerene mixtures for organic photovoltaics by systematically coarse-grained molecular simulations
Fluid Phase Equilibria, 2011; 302(1-2):21-25

© 2010 Elsevier B.V. All rights reserved.

Published at: <http://dx.doi.org/10.1016/j.fluid.2010.07.025>

PERMISSIONS

<https://www.elsevier.com/about/policies/sharing>

Preprint

- Authors can share their preprint anywhere at any time.
- If accepted for publication, we encourage authors to link from the preprint to their formal publication via its Digital Object Identifier (DOI). Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
- Authors can update their preprints on arXiv or RePEc with their accepted manuscript .

Please note:

- Some society-owned titles and journals that operate double-blind peer review have different preprint policies. Please check the journals Guide for Authors for further information
- Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles.

15 June 2021

<http://hdl.handle.net/2440/68917>

Characterization of Polymer–Fullerene Mixtures for Organic Photovoltaics by Systematically Coarse–Grained Molecular Simulations

David M. Huang, Adam J. Moule, Roland Faller

Department of Chemical Engineering & Materials Science, University of California–Davis, One Shields Ave, Davis, CA, 95616, USA

Abstract

Organic photovoltaic devices, which include polymer–based solar cells, show promise as cheap alternatives to silicon–based photovoltaics. Polymer solar cells use a mixture of a light–absorbing conducting polymer as the electron donor and a fullerene derivative as the electron acceptor in the solar cell’s photo–active layer. The components are generally mixed together to produce a bicontinuous percolating network called a bulk heterojunction. In a previous paper (Huang et al. *J. Chem. Theory Comput.* **6** (2010) 526–537) we developed a systematically coarse–grained simulation model of mixtures of the widely used conducting polymer poly(3–hexylthiophene) (P3HT) and the simplest fullerene C₆₀. Here we analyze the ensuing polymer structures and mixture morphologies to understand the local structure of these devices, which provide a crucial basis for the future optimization of bulk heterojunction morphology.

Keywords: Solar Cells, Coarse–Grained Modeling, Morphology, Polymer Structure

1. Introduction

Conjugated polymers for use in organic photovoltaic (OPV) devices are recently of high interest due to the potential for devices that are low cost, solution processable, and compatible with flexible substrates. Generally, a disordered bulk–heterojunction structure is used for the photo–active layer, which is produced when the electron donor (conjugated polymers) and the

electron acceptor (typically fullerenes) are mixed in solution and solution-cast onto a substrate [1–3]. During drying, the two species phase separate to form an interpenetrating network of domains [4, 5]. This nanoscale phase separation is crucial to device efficiency because devices need to be > 100 nm thick to absorb all incident light, but the distance over which photogenerated excitons diffuse in conjugated polymers before they are quenched is typically below 10 nm; thus only excitons generated by photons absorbed within a exciton diffusion length of a donor/acceptor interface will separate into free electrons and holes that can travel to the electrodes to generate photocurrent [6]. With a bulk heterojunction, light absorption and charge separation/transport can be optimized independently.

It has been shown that bulk-heterojunction photovoltaic devices containing mixtures of [6,6]-phenyl C_{61} -butyric acid methyl ester (PCBM) (a derivative of C_{60}) and regio-regular poly(3-hexylthiophene) (P3HT) can reach power efficiencies of up to 5% under simulated solar illumination conditions [7, 8]. The device properties hinge on the structural properties of the polymer and the polymer-fullerene mixture. The morphology and morphological changes of these devices have been studied using transmission electron microscopy [9], grazing-angle X-ray diffraction [10], atomic force microscopy [11], scanning electron microscopy [4], nuclear magnetic resonance [12], and many other experimental techniques. It turns out that P3HT forms aligned/crystalline domains, between which there are amorphous segments of P3HT and PCBM. Still, the efficiency record of about 5% for a P3HT:PCBM mixture is not competitive with the laboratory efficiency records of silicon PV devices, which are about 25% under identical lighting conditions [13]. A recent review has summed up the experimental state of the art of the morphology in these mixtures [6]. As it is clear that the efficiency of photovoltaic devices depends crucially on the morphology, it is of high interest to predict the morphology of such systems from first principles.

Molecular modeling can in principle address the morphology of phase separating systems. The fundamental limitation is, however, the achievable time and length scales in combination with the specificity of the model. All-atom simulations are not able to reach the time and length scales of phase separation in donor/acceptor mixtures used in polymer solar cells, whereas the classical models of polymer physics often lack the detail to predict the behavior of specific systems. For example, there are two different and incompatible experimental phase diagrams for P3HT:PCBM mixtures [14, 15] and models that do not realistically account for the interactions between the two

mixture components cannot possibly establish which phase diagram is the correct one. The solution to resolve the discrepancies between different experiments on a fundamental level is a mesoscale model that is uniquely linked to the specific chemistry (and thermodynamic state) of the underlying system. Several systematic techniques have been developed to map atomistic simulations structurally or based on forces onto mesoscale models [16–18]. Only very few molecular modeling studies have been performed to understand polymer photovoltaic systems [19–22] and most of these do not focus on the morphology directly.

In this article we show how a recently developed model for a mixture of fullerenes and polythiophenes [21] can be used to elucidate several important characteristics.

2. Model Building and Simulation Details

We recently developed coarse-grained (CG) models of poly(3-hexylthiophene) (P3HT), one of the most widely used semiconducting polymers in organic photovoltaics and C_{60} , the simplest fullerene, as well as for mixtures of the two materials. We have used C_{60} instead of the photovoltaically more relevant substituted fullerenes as we are focusing only on morphology prediction and not on any electrical or transport properties. Additionally, the phase separation and morphology development is expected to be more pronounced with C_{60} , as its solubility in polythiophene is lower than for other fullerenes. Systematic mapping must start with accurate atomistic simulations and a validation of the model. This was demonstrated recently by us in ref. [21], in which the development of the coarse-grained models is described in detail. The principal aspects of the model development are summarized below.

An atomistic model of P3HT was adapted from a tetrathiophene (T4) model in the literature [23]. Our model was developed for 100% regioregular P3HT (rr-P3HT), in which all monomers are joined head-to-tail. For C_{60} we used the model by Girifalco [24].

After the atomistic simulations we followed the structural coarse-graining technique known as Iterative Boltzmann Inversion (IBI) [17, 25–29]. The fullerene in the CG simulations is represented by its center of mass which coincides with the center of geometry. The P3HT monomer is represented using three sites: (1) the center-of-mass (COM) of the thiophene ring, the COM of the carbon atoms of the (2) first three and (3) last three side-chain

methyl groups [21]. Figure 1 shows the chemical structures of P3HT and C₆₀, along with the coarse-graining scheme that was used.

In the IBI method, the coarse-grained interactions are optimized by iteratively calculating the interaction energy $U_{i+1}(x)$ corresponding to a structural variable x in a given iteration from the interaction energy $U_i(x)$ in the preceding simulation and respective structural distribution using

$$U_{i+1}(x) = U_i(x) + a_i k_B T \ln \left[\frac{P_i(x)}{P_{\text{target}}(x)} \right], \quad (1)$$

where $P_i(x)$ is the probability distribution of x calculated from the CG simulation during iteration i , $P_{\text{target}}(x)$ is the target from the atomistic simulation (x can be non-bonded distance, bond length, bond angle, dihedral angle), and $0 < a_i \leq 1$ is a convergence factor. The initial interaction potential was directly from the atomistic simulation:

$$U_0(x) = -k_B T \ln [P_{\text{target}}(x)]. \quad (2)$$

After the structural optimization a linear correction,

$$\Delta U_{jk}(r) = b_{jk} \left(1 - \frac{r}{r_{\text{cut}}} \right), \quad r \leq r_{\text{cut}}, \quad (3)$$

was applied to the non-bonded interaction to correct the model so that the pressure of the CG simulations matched the 1 atm pressure used in the atomistic simulations [17, 28]. It was ensured that this correction had negligible effect on the structure (i.e. the radial distribution function for non-bonded pairs of sites was essentially unchanged).

We initially optimized the P3HT–P3HT CG interactions in pure P3HT (60 3HT 12-mers) at 550 K. Then, the P3HT–C₆₀ and C₆₀–C₆₀ CG interactions followed in simulations of 1.85:1 w/w P3HT:C₆₀ (48 3HT 12-mers and 72 C₆₀) at 550 K with the P3HT–P3HT CG interactions fixed. It has been shown that the order of optimization can make a significant difference in the overall efficiency and convergence of the procedure [27]. We ignored the end monomers in the calculation of distribution functions for the optimization. A time-step of 5 fs was used in the CG simulations and 1 fs in the atomistic simulations. Time constants of 5 and 20 ps were used respectively for the thermostat and barostat. All atomistic and CG simulations were carried out with the LAMMPS molecular dynamics simulation package [30].

Figure 1: Chemical structures of P3HT and C₆₀ with coarse-grained site types depicted and labelled.

3. Single Chain Characteristics

Having optimized the CG models in small-scale simulations, we have used them to study the dynamic evolution of P3HT:C₆₀ mixtures for experimentally relevant system sizes close to the device scale. Bulk systems of $\approx 100,000$ CG sites (corresponding to ≈ 1.2 million atoms) in a cubic simulation box of side length ≈ 25 nm were studied. Chains with degrees of polymerization $N_{\text{mono}} = 12, 24, 48,$ and 96 were treated for P3HT:C₆₀ weight ratios of 1:0, 1.85:1 and 1.27:1. All simulations were carried out in an NpT ensemble at 550 K and 1 atm, which is about 50 K above the melting point of P3HT [14] but potentially in the two-phase region for the mixtures.

One characteristic that we studied was the radius of gyration R_g which measures the sizes of the chains in the melt. For a given chain its square is defined as

$$R_g^2 = \frac{1}{N_{\text{mono}}} \sum_i^{N_{\text{mono}}} (\vec{r}_i - \vec{r}_{\text{com}})^2, \quad (4)$$

where \vec{r}_i is the position of the center of mass of monomer i and \vec{r}_{com} , is the position of the center of mass of the chain. So the radius of gyration measures the average distance from the center of mass. We can also define the gyration tensor

$$\underline{R}_g^{\alpha\beta} = \frac{1}{N_{\text{mono}}} \sum_i (\vec{r}_i - \vec{r}_{\text{com}})^\alpha (\vec{r}_i - \vec{r}_{\text{com}})^\beta, \quad (5)$$

where upper indices denote the Cartesian components. This tensor is symmetric and can therefore be diagonalized with real eigenvalues (below).

Figure 2 shows the average radius of gyration and the end-to-end distances, $R_{\text{e-e}}$, of several systems as a function of time. These measures can be taken as indications of equilibration. Most systems stabilize after at most 20 ns. Only these equilibrated systems have been analyzed further. The data in the figure is divided by the square root of the degree of polymerization as based on the Flory hypothesis [31] we expect random walks with $R_{\text{e-e}}(N_{\text{mono}}) = \sqrt{6}R_g(N_{\text{mono}}) \propto \sqrt{N_{\text{mono}}}$. The relationship between the end-to-end distance and the radius of gyration approaches the expected ratio with increasing chain length as short chains have to be classified as oligomers rather than polymers.

If we study the distribution of gyration radii (cf. Fig. 3) we immediately realize that with increasing chain length the distributions become significantly broader. We also see that the position of the maximum scales with

the square root of chain length as expected for a random walk. Moreover, especially for the longest chains we see only slight dependencies of the chain structure on the concentration of fullerenes. This already indicates that the chains and the fullerenes are separated from each other and so the fullerenes influence the polymer structure only weakly.

Another structural observable is the shape anisotropy of chains, which is defined as

$$\kappa^2 = \frac{(R_3^2 - \frac{1}{2}(R_1^2 + R_2^2))^2 + \frac{3}{4}(R_2^2 - R_1^2)^2}{R_g^4} \quad (6)$$

where $R_1^2 \leq R_2^2 \leq R_3^2$ are the eigenvalues of the gyration tensor which make up the squared radius of gyration, $R_g^2 = R_1^2 + R_2^2 + R_3^2$. $\kappa^2 = 0$ corresponds to a sphere, $\kappa^2 = 1$ to a line. This anisotropy is shown in Figure 4 to clearly decrease with chain length, which again is an indication that short chains are oligomers and not really polymers. It is known that, in general, chain anisotropy decreases with increasing chain length [32]. Again for long chains the influence of C_{60} concentration is negligible, indicating that the polymer structure is unperturbed by the fullerenes. For long chains a wide range of anisotropies is found, which shows that the chains clearly can explore many configurations and equilibration is guaranteed.

4. Characteristics of the Mixture

In order for a solar cell to work we need a structure that favors local phase separation. Our simulations are too short to find complete phase separation but the onset by virtue of local cluster formation can be studied. We have followed the growth of fullerene clusters over the course of our CG simulations. We see that over a time scale of a few tens of nanoseconds there is clearly a cluster formation for the 1.27:1 w/w mixture, indicating that at 550 K this ratio is in the two-phase region. We do not find significant clustering for the lower fullerene concentration in the 1.85:1 w/w mixture, for which the largest cluster remains small and does not grow with time such that this ratio is in the homogeneous phase. It appears that in the two-phase region the cluster formation speed is chain length independent (cf. Fig. 5). As shown in Fig. 6, we also find that the clusters are not spherical but have a large surface area and, by visual inspection of the simulation snapshots in this figure, that the domain size is on the order of the exciton diffusion length ≈ 10 nm. In the example case of 48-mers in the 1.27:1 w/w mixture, after 135 ns most of the C_{60} in our simulation belongs to the largest cluster in the system and we

Figure 2: $\langle R_g^2/N_{\text{mono}} \rangle^{1/2}$ (solid lines) and $\langle R_{e-e}^2/(6N_{\text{mono}}) \rangle^{1/2}$ (dashed lines) as a function of time, where R_g , R_{e-e} , and N_{mono} are the radius of gyration, end-to-end distance, and degree of polymerization of the chains, respectively, starting from a pseudo-random configuration of polymer chains and C_{60} molecules, for various P3HT: C_{60} blend ratios and polymer chain lengths: P3HT: C_{60} = 1:0 w/w with $N_{\text{mono}} = 24$ (crosses) and $N_{\text{mono}} = 48$ (circles), P3HT: C_{60} = 1.85:1 w/w with $N = 48$ (squares), and P3HT: C_{60} = 1.27:1 w/w with $N_{\text{mono}} = 12$ (up triangles), $N_{\text{mono}} = 24$ (down triangles), and $N_{\text{mono}} = 48$ (diamonds). The temperature T is 550 K in all cases.

Figure 3: Probability distribution $p(R_g)$ for various P3HT:C₆₀ blend concentrations and chain lengths: P3HT:C₆₀ = 1:0 w/w with $N_{\text{mono}} = 48$ (circles) and P3HT:C₆₀ = 1.27:1 w/w with $N_{\text{mono}} = 12$ (up triangles), $N_{\text{mono}} = 24$ (down triangles), and $N_{\text{mono}} = 48$ (diamonds). (Only distributions for systems in Fig. 2 for which simulations were run long enough for $p(R_g)$ to become constant with time are shown.)

Figure 4: Probability distribution $p(\kappa^2)$ of polymer chain shape anisotropy for various P3HT:C₆₀ blend ratios and polymer chain lengths: P3HT:C₆₀ = 1:0 w/w with $N_{\text{mono}} = 48$ (circles) and P3HT:C₆₀ = 1.27:1 w/w with $N_{\text{mono}} = 12$ (up triangles), $N_{\text{mono}} = 24$ (down triangles), and $N_{\text{mono}} = 48$ (diamonds). The temperature is 550 K. (Only distributions for systems where equilibration could be ensured are shown.)

clearly see percolation, which is a desired morphology as continuous paths of both the polymer and the fullerene phase to the corresponding electrodes are needed to generate photocurrent.

We should point out that, since the CG models were optimized for the fluid structure and not for the dynamics, the times scales for dynamics in the CG simulations are not necessarily equivalent to those in the atomistic simulations. Comparing these time scales from first principles is not a simple task. From our previous work in which we developed the CG models of P3HT and C_{60} [21], we estimated that the coarse-grained time scale is roughly one to five times the atomistic time scale by comparing the translational diffusion coefficients of P3HT 12-mers and C_{60} and rotational diffusion coefficients of P3HT in equivalent atomistic and coarse-grained systems for different mixture ratios and temperatures between 500 and 650 K. Thus, although the CG time scales in our simulations are not directly comparable with the "real" time scales, our previous results suggest that these time scales are likely of the same order of magnitude.

5. Conclusions

We show that our recently developed systematically coarse-grained model of fullerene-polythiophene mixtures can describe the local morphology in bulk heterojunctions on the length scales of several tens of nanometers, close to the photovoltaically relevant scale. The phase separation and cluster formation agrees reasonably with experimental expectations on the scale of the phase separating domains. Very large-scale simulations will in the future be able to describe the morphology over several fullerene and thiophene domains. Currently we can describe the phase separation qualitatively but with increasing model quality we expect a more quantitative description of the phase transition temperatures in the future.

Acknowledgements

This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

- [1] J. J. M. Halls, C. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, Efficient photodiodes from interpenetrating polymer networks, *Nature* 376 (6540) (1995) 498–500.

Figure 5: The number of C_{60} molecules in the largest C_{60} cluster in the system, $N_{\text{cluster,max}}$, as a function of time for various P3HT: C_{60} blend ratios and polymer chain lengths: P3HT: C_{60} = 1.85:1 w/w with $N_{\text{mono}} = 48$ (squares) and P3HT: C_{60} = 1.27:1 w/w with $N_{\text{mono}} = 12$ (up triangles), $N_{\text{mono}} = 24$ (down triangles), and $N_{\text{mono}} = 48$ (diamonds). Two C_{60} molecules are in the same cluster if their centers are closer than $r_{\text{cl}} = 10.2 \text{ \AA}$.

Figure 6: Snapshots of the simulation configuration of the system with P3HT:C₆₀ = 1.27:1 w/w with $N_{\text{mono}} = 48$ at $t = 0$ ns (left), $t = 30$ ns (center), and $t = 135$ ns (right). The C₆₀ molecules in the largest cluster are highlighted in blue and all other particles in the system shown as dots. The length of each side of the simulation box is roughly 25 nm.

- [2] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Polymer photovoltaic cells – enhanced efficiencies via a network of internal donor-acceptor heterojunctions, *Science* 270 (5243) (1995) 1789–1791.
- [3] K. M. Coakley, M. D. McGehee, Conjugated polymer photovoltaic cells, *Chemistry of Materials* 16 (23) (2004) 4533–4542.
- [4] H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner, N. S. Sariciftci, Nanoscale morphology of conjugated polymer/fullerene-based bulk-heterojunction solar cells, *Adv. Funct. Mater.* 14 (10) (2004) 1005–1011.
- [5] J. K. J. van Duren, N. X. Yang, J. Loos, C. W. T. Bulle-Lieuwma, A. B. Sieval, J. C. Hummelen, R. A. J. Janssen, Relating the morphology of poly(p-phenylene vinylene)/methanofullerene blends to solar-cell performance, *Adv. Funct. Mater.* 14 (5) (2004) 425–434.
- [6] R. Giridharagopal, D. S. Ginger, Characterizing morphology in bulk heterojunction organic photovoltaic systems, *J Phys Chem Lett* 1 (7) (2010) 1160–1169.
- [7] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends, *Nature Materials* 4 (11) (2005) 864–868.

- [8] M. Reyes-Reyes, K. Kim, D. L. Carroll, High-efficiency photovoltaic devices based on annealed poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C-61 blends, *Applied Physics Letters* 87 (8) (2005) 083506.
- [9] X. N. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels, R. A. J. Janssen, Nanoscale morphology of high-performance polymer solar cells, *Nano Letters* 5 (4) (2005) 579–583.
- [10] T. Erb, U. Zhokhavets, G. Gobsch, S. Raleva, B. Stuhn, P. Schilinsky, C. Waldauf, C. J. Brabec, Correlation between structural and optical properties of composite polymer/fullerene films for organic solar cells, *Adv Funct Mater* 15 (7) (2005) 1193–1196.
- [11] R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. S. Liu, J. M. J. Frechet, M. F. Toney, Dependence of regioregular poly(3-hexylthiophene) film morphology and field-effect mobility on molecular weight, *Macromolecules* 38 (8) (2005) 3312–3319.
- [12] C. Y. Yang, J. G. Hu, A. J. Heeger, Molecular structure and dynamics at the interfaces within bulk heterojunction materials for solar cells, *J Am Chem Soc* 128 (36) (2006) 12007–12013.
- [13] Department of Energy, Basic research needs for solar energy utilization, Tech. rep. (2005).
- [14] C. Müller, T. A. M. Ferenczi, M. Campoy-Quiles, J. M. Frost, D. D. C. Bradley, P. Smith, N. Stingelin-Stutzmann, J. Nelson, Binary organic photovoltaic blends: A simple rationale for optimum compositions, *Advanced Materials* 20 (18) (2008) 3510–3515.
- [15] J. Y. Kim, C. D. Frisbie, Correlation of phase behavior and charge transport in conjugated polymer/fullerene blends, *J Phys Chem C* 112 (45) (2008) 17726–17736.
- [16] S. Izvekov, G. A. Voth, A multiscale coarse-graining method for biomolecular systems, *J Phys Chem B* 109 (7) (2005) 2469–2473.

- [17] D. Reith, M. Pütz, F. Müller-Plathe, Deriving effective meso-scale coarse graining potentials from atomistic simulations, *J Comput Chem* 24 (13) (2003) 1624–1636.
- [18] H. Meyer, O. Biermann, R. Faller, D. Reith, F. Müller-Plathe, Coarse graining of nonbonded interparticle potentials using automatic simplex optimization to fit structural properties, *J. Chem. Phys.* 113 (15) (2000) 6264–6275.
- [19] D. Cheung, D. McMahon, A. Troisi, Computational study of the structure and charge-transfer parameters in low-molecular-mass P3HT, *J Phys Chem B* 113 (28) (2009) 9393–9401.
- [20] D. Cheung, D. McMahon, A. Troisi, A realistic description of the charge carrier wave function in microcrystalline polymer semiconductors, *J Am Chem Soc* 131 (31) (2009) 11179–11186.
- [21] D. M. Huang, R. Faller, K. Do, A. J. Moule, Coarse-grained computer simulations of polymer/fullerene bulk heterojunctions for organic photovoltaic applications, *J Chem Theor Comp* 6 (2) (2010) 527–537.
- [22] M. Moreno, M. Casalegno, G. Raos, S. Meille, R. Po, Molecular modeling of crystalline alkylthiophene oligomers and polymers, *J Phys Chem B* 114 (4) (2010) 1591–1602.
- [23] V. Marcon, G. Raos, Free energies of molecular crystal surfaces by computer simulation: Application to tetrathiophene, *J Am Chem Soc* 128 (5) (2006) 1408–1409.
- [24] L. A. Girifalco, Molecular properties of fullerene in the gas and solid phases, *J Phys Chem* 96 (2) (1992) 858–861.
- [25] Q. Sun, R. Faller, Crossover from unentangled to entangled dynamics in a systematically coarse-grained polystyrene melt, *Macromolecules* 39 (2) (2006) 812–820.
- [26] Q. Sun, R. Faller, Phase separation in polyisoprene/polystyrene blends by a systematically coarse-grained model, *J Chem Phys* 126 (14) (2007) 144908.

- [27] Q. Sun, R. Faller, Systematic coarse-graining of a polymer blend: Polyisoprene and polystyrene, *J Chem Theor Comp* 2 (3) (2006) 607–615.
- [28] R. Faller, Coarse-grain modeling of polymers, in: K. B. Lipkowitz, T. R. Cundari, D. B. Boyd (Eds.), *Reviews in Computational Chemistry*, Vol. 23, Wiley-VCH, Hoboken, New Jersey, 2007, Ch. 4, pp. 233–262.
- [29] Q. Sun, J. Ghosh, R. Faller, State point dependence and transferability of potentials in systematic structural coarse-graining, in: G. Voth (Ed.), *Coarse-Graining of Condensed Phase and Biomolecular Systems*, Chapman and Hall/CRC Press, Taylor and Francis Group, 2008, Ch. 6, pp. 69–82.
- [30] S. J. Plimpton, Fast parallel algorithms for short-range molecular dynamic, *J Comp Phys* 117 (1) (1995) 1–9.
- [31] M. Doi, S. F. Edwards, *The Theory of Polymer Dynamics*, Vol. 73 of International Series of Monographs on Physics, Clarendon Press, Oxford, 1986.
- [32] D. N. Theodorou, U. W. Suter, Shape of unperturbed linear polymers: polypropylene, *Macromolecules* 18 (6) (1985) 1206–1214.