

A new general model with non-spherical interactions for dense polymer systems and a potential parametrization for Bisphenol-A-Polycarbonate

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Abstract

We introduce a new general model for the simulation of dense macromolecular systems. It consists of basic ellipsoidal shaped units stringed together to form chains, including branched and side chains. The ellipsoidal shaped unit can vary in its principal axes and degenerate to a sphere, allowing for flexible modeling of the monomer units. We apply the model to the special case of Bisphenol-A-Polycarbonate (BPA-PC) and present a parametrization for the intra- and intermolecular potentials. We use a mere repulsive potential to model the non-bonded interactions. Using the developed model potentials we present at the meeting data on the thermodynamic properties of polycarbonate systems. We will also present properties and efficiency considerations of the ellipsoidal model.

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1 Introduction

The starting point for our model is the coarse-graining ansatz as developed by Paul et al [5, 6, 13]. To present the model along with an application to a specific material, we describe the approach for the Bisphenol-A-Polycarbonate (BPA-PC) and a variation of the polycarbonate.

In the coarse-graining approach we want to map larger units of the realistic chain onto one or more units of a new chain such that the interactions between the new units reflect and mimic those of the chemically realistic chain. The units we map can be the repeating unit of the chain, or parts of the repeating unit. The decision on the size or which atoms take part in one unit can be based on the coherence and persistence length of the chain.

Consider three atoms bonded to form a simple chain. We want to keep for example the average end-to-end distance or the radius of gyration invariant. The possible variation in the monomer lengths and the monomer angles between the three atoms can be well-represented by just two atoms with rescaled monomer length and monomer angle potentials if we also rescale the zero-temperature monomer length and monomer angle.

Once the length scale is fixed, atoms of the unit are taken as base points. From the possible conformations of the chain we find the distributions for the *monomer lengths* and *monomer angles* between the base points along the chemically realistic chains. The distribution contains information on the local structure on scales smaller than the fixed length scale.

To develop a coarse-grained model monomer (in our case for BPA-PC) we proceed in three steps. As input we use the results of ab-initio calculations of the geometry and the torsional potentials. Furthermore we use monomer length and monomer angle distributions that have been determined via Monte-Carlo simulations from the ab-initio results [14].

1. We compute a discrete potential around one resp. two atomistic monomer units.
2. From the distributions mentioned above we determine the *bonded* coarse-grained interactions.
3. From the results of 1. we determine the *non-bonded* coarse-grained interaction constants.

One caveat to this approach must be mentioned here. The chains generated by the Monte-Carlo procedure are in vacuum. The intermolecular interaction and its effect on the chain conformations is not taken into account. Only intramolecular interactions are used for the generation of the conformations so far. In principle an intermolecular interaction can be worked into the generation of the conformations.

The ab-initio calculations mentioned above show that in the case of Bisphenol-A-Polycarbonate, which is regarded here, the torsional potential is neglectable.

Thus we introduce no torsional interaction. In general, torsional interaction must and can be included.

2 The monomer unit

Our approach starts from the general ellipsoid model for the description of polymer chains [17]. In this model the basic building block is an ellipsoid. Up to now our monomers show rotational symmetry along the backbone. Symmetry-breaking *side-groups* can be modeled by sticking degenerate ellipsoids (spheres) to the main ellipsoids. Of course, the ellipsoid itself need not be rotationally symmetric. We can also use oblate ellipsoids and in general ellipsoids with all three principal axes different. This, however, makes the calculation of the non-bonded interaction more difficult.

An ellipsoid can easily be adapted to different monomer structures. We only have to change the half-axes and radii according to the size of the chemically realistic monomers. In the simplest form we have no side groups at all and the chain consists of rotational ellipsoids whose longer half axes can assume values according a given *monomer length* distribution. The position of the monomers along the same chain is furthermore determined by the *monomer angles*. The short half-axes are chosen so that the volume of the ellipsoids corresponds, in the case of BPA-PC, to the volume of the chemical monomer unit.

In the following, we describe the procedure to obtain the bonded interaction potentials for the case of Bisphenol-A-Polycarbonate. After that the geometric shape of the monomers and the non-bonded intermolecular potentials are determined.

3 Bonded Interactions for BPA-PC

The bonded potentials for the length of the monomer units and the angle between two of them are obtained in our approach from a coarse-graining procedure [13]. No torsion potential is needed, as the distribution of torsion angles is almost uniform. The result of the coarse-graining is a distribution of lengths and angles between the new building blocks. The input for the determination of the coupling is the distribution of lengths (angles) of chemically detailed monomer units [14] This distribution is obtained from a generation of chains with the detailed chemistry and interaction using Monte-Carlo simulations and shows two clear peaks. It must be kept in mind however, that the distribution does not contain effects from the packing and intermolecular interaction in a dense system. Consistent with this we may view these interactions as given by a sum of gaussians. The correlations between monomer length and angle and intermolecular interaction are neglected and the coupling constants simply determined from the second

moments of the distributions.

In our case of BPA-Polycarbonate we used an average distribution for the backbone atoms of the carbonate-group (see section 4), i.e. the center of mass of the atoms labelled O_1 , C_1 and O_2 of one monomeric unit and the corresponding center of mass of the succeeding monomeric unit (see fig 1). The carbonate-groups may be regarded as joints along the polymer chain.

Performing a simultaneous fit of two gaussians to the monomer length distribution as described in [14] we obtain the four parameters

$$\langle l_{01} \rangle \quad \text{and} \quad \langle l_{01}^2 \rangle \quad (1)$$

$$\langle l_{02} \rangle \quad \text{and} \quad \langle l_{02}^2 \rangle \quad (2)$$

$$(3)$$

representing the two average monomer lengths ($\langle l_{01} \rangle$ and $\langle l_{02} \rangle$) and the two variances ($\langle l_{01}^2 \rangle$ and $\langle l_{02}^2 \rangle$) characterizing the width of the distributions. For simplification, no crossing of monomers between the two distributions is permitted. The distributions are temperature dependent and the fitting must be carried out for each simulation temperature independently.

Along the same line the parameters for the monomer angle distribution

$$\langle \theta_0 \rangle \quad \text{and} \quad \langle \theta_0^2 \rangle \quad (4)$$

are obtained from the fit of a single gaussian [14].

These parameters must be fitted to the parameters of the model Hamiltonian

$$\begin{aligned} \mathcal{H}_{\text{bond}} = & \frac{1}{2}k_1 \sum_i s_i (l_i - l_{01})^2 + \\ & \frac{1}{2}k_2 \sum_i (1 - s_i) (l_i - l_{02})^2 + \end{aligned} \quad (5)$$

$$\frac{1}{2}k_\theta \sum_i (\cos \theta_i - \cos \theta_0)^2 \quad (6)$$

where s_i is 1 for monomers belonging to the first distribution (l_{01}) and 0 for monomers of the second distribution (l_{02}). Analysis of cross-correlations between monomer length and monomer angle distributions reveals that they can be neglected. Therefore as a first approximation we identify $\langle l_{0i} \rangle$ with l_{0i} and $k_B T / \langle l_{0i}^2 \rangle$ with k_i .

This form of interaction has already been used in other models for Polyethylene [10] and BPA-Polycarbonate [5, 6, 7, 8, 9]. An a-posteriori test of the distribution using simulated systems confirm the correctness of this ansatz. The simulations led to distributions that indeed showed the skewed form of the ab-initio distribution.

4 Non-bonded interactions for BPA-PC

The input for the development of the potential within the ellipsoidal model is a quantum-chemical ab-initio calculation. This calculation yields data on

- the geometry of a monomer unit of BPA-PC,
- a discretization of the potential around the monomer unit.

These and the van-der-Waals radii of the respective atoms are the input for the determination of the size of the monomer unit as represented by an ellipsoid and the inter-molecular potential. To illustrate that indeed the approximation of an ellipsoid with rotational symmetry is a good choice, we show in figure 2 the isopotential lines for a cut perpendicular to the principal axis of the BPA-PC monomer.

To reduce the numerical complexity of the model as presented in [17] we concentrated the whole mass of the monomer in the focal points. So we don't really have to integrate along the backbone (as described in [17]) but can reduce the interaction between two ellipsoids \mathcal{A} and \mathcal{B} to a sum of four interactions:

$$\begin{aligned} \mathcal{H}_{\text{non-bond}} &= \sum_{\mathcal{A}, \mathcal{B}} V_{\mathcal{A}\mathcal{B}} & (7) \\ V_{\mathcal{A}\mathcal{B}} &= V(\mathcal{A}, \vec{f}_1^{\mathcal{B}}) + V(\mathcal{A}, \vec{f}_2^{\mathcal{B}}) \\ &+ V(\mathcal{B}, \vec{f}_1^{\mathcal{A}}) + V(\mathcal{B}, \vec{f}_2^{\mathcal{A}}) \end{aligned}$$

Here $V(\mathcal{M}, \vec{p})$ indicates the three-point interaction between the monomer \mathcal{M} , i.e. its both focal points $\vec{f}_i^{\mathcal{M}}$, $i = 1, 2$, and the point \vec{p} .

$V(\mathcal{M}, p)$ is defined as follows:

$$\begin{aligned} V(\mathcal{M}, \vec{p}) &= V_{\text{rep}}(r_p) \\ r_p &= \frac{1}{2} \left(|\vec{p} - \vec{f}_1^{\mathcal{M}}| + |\vec{p} - \vec{f}_2^{\mathcal{M}}| - |\vec{f}_1^{\mathcal{M}} - \vec{f}_2^{\mathcal{M}}| \right) & (8) \end{aligned}$$

$$\sigma = a_{\sigma}^{\mathcal{M}} - \frac{1}{2} |\vec{f}_1^{\mathcal{M}} - \vec{f}_2^{\mathcal{M}}| + r_{\sigma}^p \quad (9)$$

where $a_{\sigma}^{\mathcal{M}}$ is the long half-axis of the ‘‘excluded ellipsoid’’ confocal to \mathcal{M} , and r_{σ}^p is the radius of the ‘‘excluded sphere’’ around the point \vec{p} . The potential around \mathcal{M} decreases confocally (fig. 3).

For the potential $V_{\text{rep}}(r_p)$ we assume a merely repulsive interaction

$$\begin{aligned} V_{\text{rep}}(r) &= \begin{cases} V_6(r) - V_6(r_c) - (r - r_c) \frac{\partial}{\partial r_c} V_6(r_c) & \text{for } \sigma < r < r_c \\ \infty & \text{for } r < \sigma \\ 0 & \text{for } r > r_c \end{cases} & (10) \\ V_6(r) &= \epsilon(r - \sigma)^{-6} \end{aligned}$$

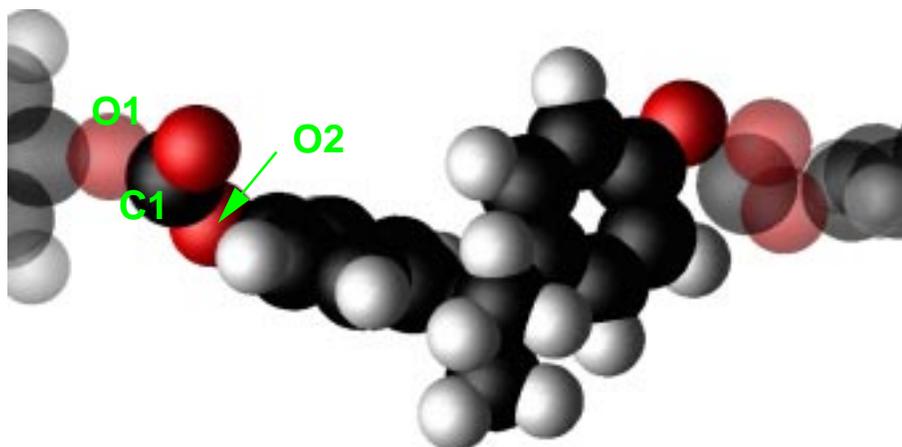


Figure 1: Position of atoms in the BPA-PC monomer. Two adjacent monomers are shown.

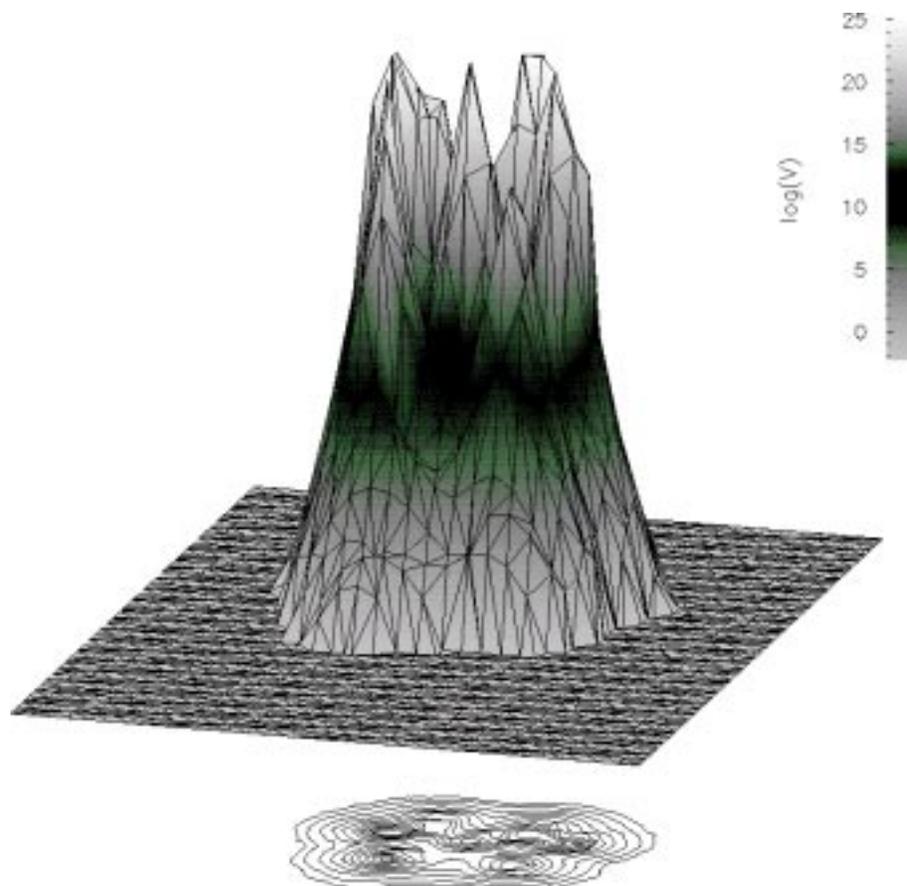


Figure 2: Isopotential lines for a cut perpendicular to the principal axis of the BPA-PC monomer.

with initially two free parameters, σ for the excluded volume and ϵ which sets the energy scale. The cut-off r_c is determined from the zero-potential iso-surface.

We reduce the non-bonded interaction to a mere excluded volume interaction. In order to have a short-range potential that does not force us to chose too small time steps we use a simple r^{-6} -repulsion. The discrete potential of the chemically detailed monomer mentioned above shows that in the case of polycarbonate the strength of the attractive part of the potential is very small. Thus we neglect any attractive interaction for computational reasons.

5 Summary

We have introduced a new general model for dense polymer systems which allows for simulating dense polymer systems at a coarse-grained level. Simple basic constituents like ellipsoids and spheres can be stucked together to build complex polymer structures. For this model we have presented a parameterization of Bisphenol-A-Polycarbonate. The Hamiltonian considered here is a sum of bonded and non-bonded interactions. The bonded interactions are modelled by harmonic spring potentials, the non-bonded interaction is given as a mere repulsive r^{-6} -potential. We introduced some simplifications to the model which reduce the numerical effort but have hardly any influence on the advantages of this new general ansatz. We are currently running simulations using the ellipsoid model with these parametrizations and simplifications to evaluate the dynamical behaviour of a dense BPA-PC system coarse-grained due to our model. These will be presented at the meeting.

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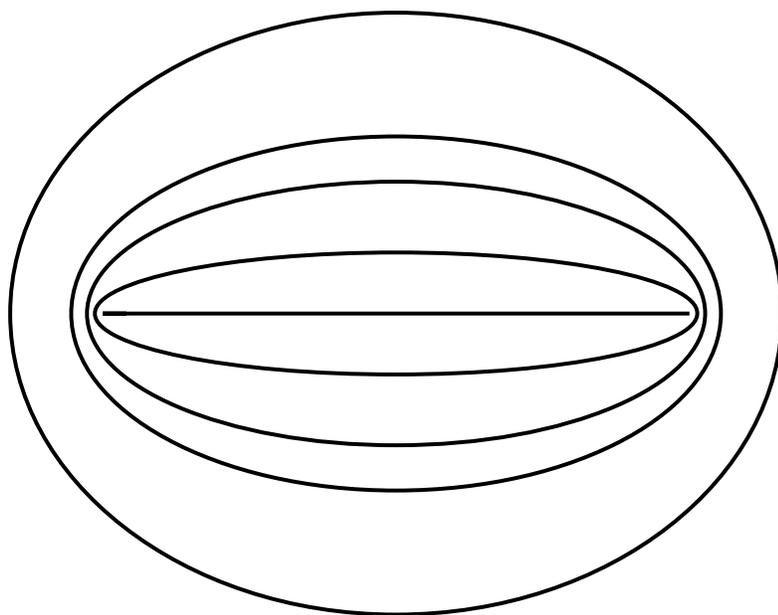


Figure 3: The intermolecular potential decreases confocally