Ellipsoidal Potential Parameterization for Bisphenol–A–Polycarbonate

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Abstract

We present a coarse-grained parameterization for the intra- and intermolecular potential for Bisphenol-A-Polycarbonate (BPA-PC). The parameterization is based on the ellipsoidal shaped monomer unit model applied to BPA-PC. Because of the symmetries of the model a Lennard-Jones type or even a mere repulsive potential with the usual parameters suffices to model the non-bonded interactions. We determine the potential parameters from ab-initio quantum calculations for the BPA-PC monomer.
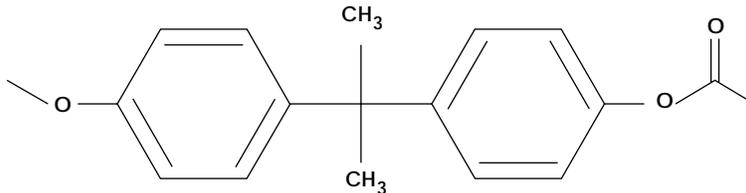
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Figure 1: Schematic representation of a monomer unit of Bisphenol-A-Poly-carbonate (BPA-PC).

1   Introduction

In this paper we would like to describe the modelling of a potential for the simulation of dense polymer systems. Many different points of view have been taken on this issue (for two recent reviews see [1]). These may be partitioned into atomistic and coarse-grained.

In the atomistic approach one tries to keep the detailed chemistry. A potential model is then assumed which takes into account the detailed interaction between all the atoms. A recent example for a parameterization of a polycarbonate was given by Sun *et. al.*[2]. Such a chemically-realistic description may be very well used for short, single chains. For long and many chains the computational complexity soon becomes overwhelming. Thus it is necessary to reduce the complexity of the calculations to allow the simulation of dense macromolecular systems.

In the coarse-grained approach the detailed chemistry enters only in the derivation of the potential between new interacting units [5]. These are substitutes for the original detailed chemistry. The system is considered on large length and longer time scales. Loosely speaking the fast degrees of freedom, like the bond vibrations have been eliminated and the short spatial length scales have been upscaled.

Our potential model is of the second type and here we focus our attention on the application to a glassy macromolecular system of the polycarbonate type. Specifically, we derive the parameters for the Bisphenol-A-Polycarbonate (BPA-PC, see figure 1).

Our approach starts from a general model for the description of polymer chains [3]. In this model the basic building block is an ellipsoid. Using this building block chains can be constructed, may they be linear chains, chains with side chains or branched. Because the ellipsoid can degenerate into a sphere, our approach is able to accomodate and model even complex and asymmetric monomer units in a rather simple way. An example is shown in figures 3 for the Trimethylcyclohexan-Polycarbonate (TMC-PC) (see figure 2) with additional spheres attached to the ellipsoids to take into account the side group [4].

In comparison to the bond-fluctuation model on the lattice or the bead-spring model in the continuum the main advantages of the ellipsoidal model are its
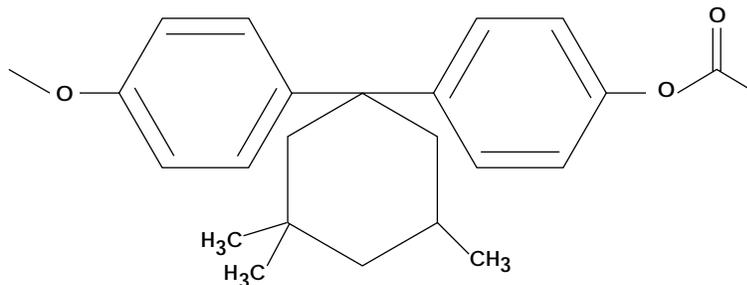
Figure 2: Schematic representation of a monomer unit of Trimethylcyclohexan-Polycarbonate (TMC-PC).
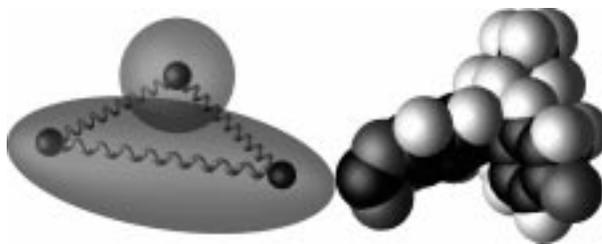

Figure 3: Schematic representation of the modelling of TMC-PC within the ellipsoidal model

geometric flexibility and the fact that the excluded volume of any chemically realistic polymer can be preserved so that the detailled atomic structure may easily be reinserted.

Given the basic building block we model the Bisphenol-A-Polycarbonate by a string of ellipsoids with rotational symmetry along the principal axis (figure 4). In order not to increase the computational complexity unnecessarily no side groups in the form of e. g. spheres are attached to the ellipsoid. This can be justified by the fact that the BPA-Polycarbonate shows only a slight curvature within its monomer unit and, as an acceptable approximation, can be regarded as rotational symmetric.

To develop a coarse-grained model of a Bisphenol-A-Polycarbonate (BPA-PC) monomer we proceeded in four steps. As input we used the results of ab-initio calculations of the geometry and the torsional potentials.

1. We performed Monte-Carlo simulations on an atomistic level to determine the monomer-length and monomer-angle distributions.

2. We computed the potential on a grid around one resp. two atomistic monomer units.

3. From the distributions mentioned in 1., we determine the *bonded* coarse-grained interactions.
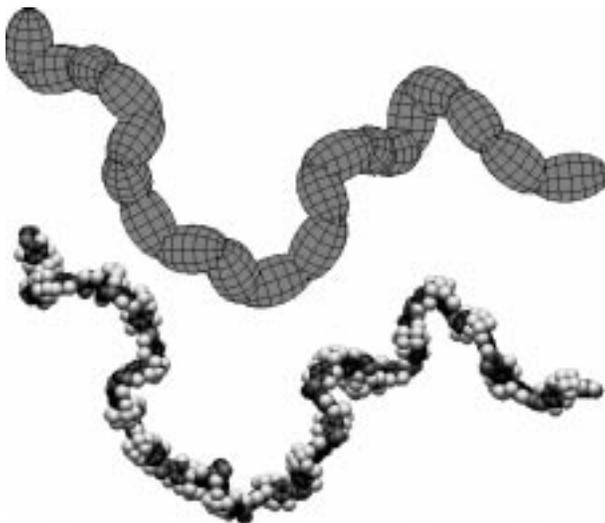
Figure 4: Modelling of a BPA-PC chain within the ellipsoidal model

4. From the results of 2. we determine the *non-bonded* coarse-grained interaction constants.

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

2 Bonded Interactions

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 [5]. 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 detailled monomer units (cf. figure 5). This distribution is obtained from a generation of chains with the detailed chemistry and interaction using Monte-Carlo simulations. It must be kept in mind however, that the distribution does not contain effects from the packing and intermolecular interaction in a dense system. This MC-calculation resembles a RIS-calculation with interdependent potentials. The only difference to the classical RIS-approach is that torsions are not restricted to discrete values. The correlations between bond 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 3), i.e. the center of mass of
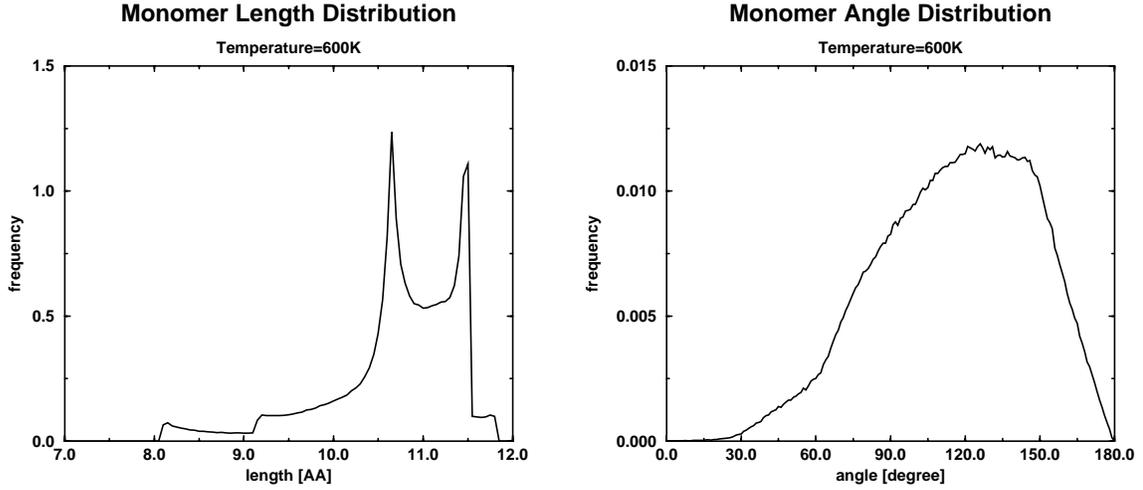
Monomer Length Distribution

Temperature=600K

Monomer Angle Distribution

Temperature=600K

Figure 5: Bond length and bond angle distributions of BPA-PC monomers at T=600 K. The distributions refer to the center of mass of the carbonate-group.

the atoms labelled O_1, C_1 and O_2 of one monomeric unit and the corresponding center of mass of the succeding monomeric unit (see fig 6). The carbonate-groups may be regarded as joints along the polymer chain.

From a simultaneous fit of two gaussians to the bond length distribution of figure 5 we obtain the four parameters

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

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

$$\tag{3}$$

representing the two average bond 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 bond angle distribution

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

are obtained from the fit of a single gaussian.

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

$$\mathcal{H}_{\text{bond}} \quad = \quad \frac{1}{2} k_1 \sum_i s_i (l_i - l_{01})^2 +$$

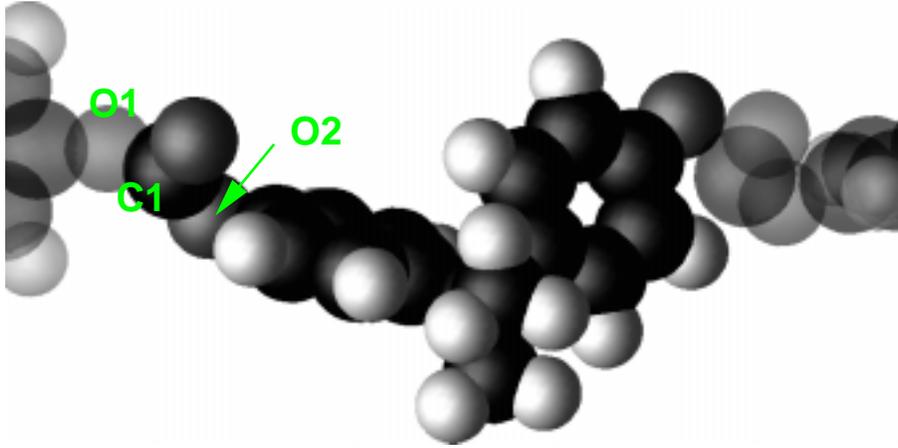$$\frac{1}{2} k_2 \sum_i (1 - s_i)(l_i - l_{02})^2 + \tag{5}$$

Figure 6: Position of atoms in the BPA-PC monomer. Two adjacent monomers are shown.

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

(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 bond length and bond 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.

3 Non-bonded interactions

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 on a 6-31G basis set level,

- 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 7 the isopotential lines for a cut perpendicular to the principal axis of the BPA-PC monomer.

To fix the position and orientation of the quantum-chemical monomer in the set of discrete potential values we determined the vector between the center of
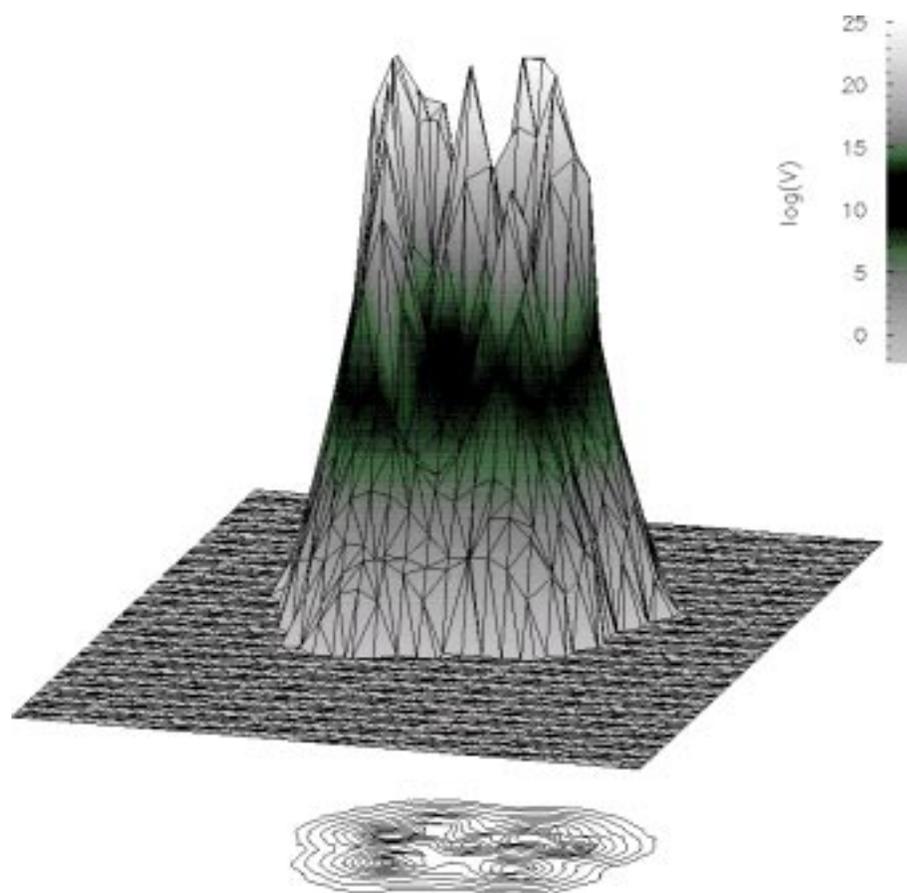
Figure 7: Isopotential lines for a cut perpendicular to the principal axis of the BPA-PC monomer.
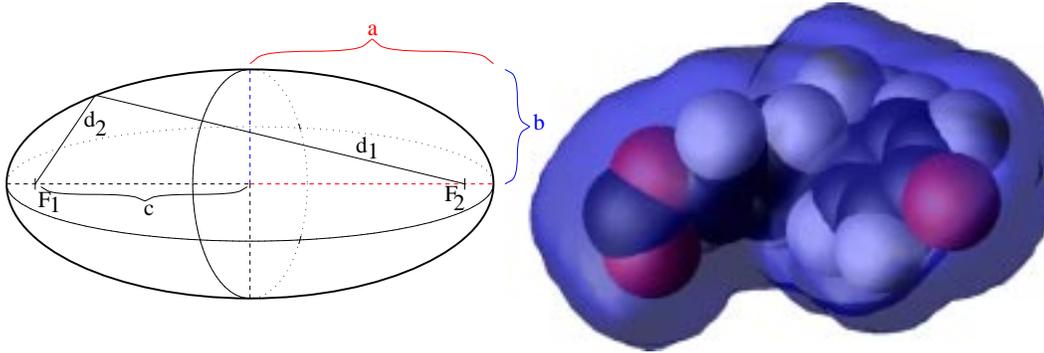
Figure 8: Ellipsoid constants and an illustration of the isosurface for the excluded volume of an isolated monomer.

mass of the atoms labeled O_1, C_1 and O_2 of one monomeric unit and the corresponding center of mass of the succeding monomeric unit (see fig 6). This choice is dictated first by the chosen bond-length and bond-angle coarse-graining procedure and by the principal axis of the tensor of the moments of inertia of the chemical monomer. An analysis of this tensor reveals that the long principal axis is parallel to the vector between the centers of mass.

The magnitude of the vector connecting the centers of mass determines the length of our reference monomer unit for the Bisphenol-A-Polycarbonate monomer ($l \approx 11.2\,\text{Å}$). This is in good agreement with the peaks in the bond length distribution (see fig 5), where we have $l_0 = 10.65\,\text{Å}$ and $l_1 = 11.5\,\text{Å}$.

The next step is the determination of the long and short half-axis for the ellipsoidal model. First we determined the volume v_1 of the real BPA-PC inside the isosurface $U = 0$, i.e. the excluded volume of an *isolated* monomer unit interacting with a test atom. In our case the test atom is a carbon atom.

We now computed the long and short half-axis (a and b respectively) of an ellipsoid with the same volume $v = v_1$ and the distance l between the focal points. This ellipsoid has rotational symmetry around the long half-axis.

We have

$$v = \frac{4\pi}{3}ab^2 \quad \text{and} \quad a^2 - b^2 = c^2 \tag{7}$$

where $c = 0.5 \cdot l$ is the half distance between the two focal points (cf. fig 8) and l is the length of the monomer unit as calculated by the above outlined procedure. Thus we have the cubic equation

$$a^3 - ac^2 - \frac{3v}{4\pi} = 0. \tag{8}$$

which gives with $v = v_1 = 751.734$ and $c = 5.583$

$$a = 7.44\text{Å} \qquad \text{and} \qquad b = 4.91\text{Å} \tag{9}$$
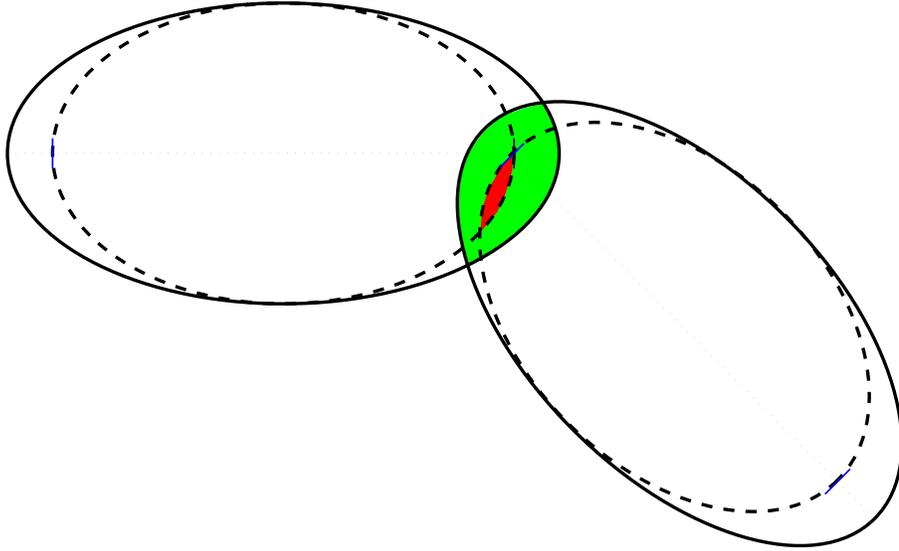
for our reference monomer.

Figure 9: Two models of fitting ellipsoids onto one another. In the non-overlapping model, neighbour monomers are connected at the surface. In the overlapping model, monomers are connected at their focal points.

We now have determined the short half axis of the ellipsoid, i.e. the "thickness" of the monomer. For the length we may either use $2 \cdot a$ which involves a rather big overlap with neighbour monomers at each end but gives quite a good approximation of the real monomer unit. Or we may use $l = 2 \cdot c$, where the overlap may be neglected. The first model connects monomers at the focal points (see figure 9) while the latter model connects the ellipsoids at their surface. However, in this case the monomers can go into a disc-like state during the simulation with a complex distance between the focal points. Thus the advantage of a vanishing overlap is annihilated by the need of additional constraints in order to prevent the monomer from becoming oblate.

We thus obtained the following parameters for the ellipsoid:

overlapping version	non-overlapping version	values
a_o	—	$7.44\,\text{Å}$
b_o	b_n	$4.91\ \text{Å}$
c_o	a_n	$5.58\,\text{Å}$
—	$c_n = \sqrt{a_n^2 - b_n^2}$	2.65Å

To reduce the numerical complexity of the model as presented in [3] 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 [3]) but can reduce the

interaction between two ellipsoids $\mathcal{A}$ and $\mathcal{B}$ to a sum of four interactions:

$$\mathcal{H}_{\text{non-bond}} = \sum_{\mathcal{A},\mathcal{B}} V_{\mathcal{A}\mathcal{B}} \tag{10}$$

$$V_{\mathcal{A}\mathcal{B}} = V(\mathcal{A}, \vec{f}_1^{\mathcal{B}}) + V(\mathcal{A}, \vec{f}_2^{\mathcal{B}})$$
$$+ V(\mathcal{B}, \vec{f}_1^{\mathcal{A}}) + V(\mathcal{B}, \vec{f}_2^{\mathcal{A}})$$

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:

$$V(\mathcal{M}, \vec{p}) = V_{\text{rep}}(r_p)$$
$$r_p = \frac{1}{2}\left(\left|\vec{p} - \vec{f}_1^{\mathcal{M}}\right| + \left|\vec{p} - \vec{f}_2^{\mathcal{M}}\right| - \left|\vec{f}_{1,\mathcal{M}} - \vec{f}_2^{\mathcal{M}}\right|\right) \tag{11}$$
$$\sigma = a_{\sigma}^{\mathcal{M}} - \frac{1}{2}\left|\vec{f}_1^{\mathcal{M}} - \vec{f}_2^{\mathcal{M}}\right| + r_{\sigma}^p \tag{12}$$

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 $\vec{p}$.

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

$$V_{\text{rep}}(r) = \begin{cases} V_6(r) - V_6(r_c) - (r - r_c)\frac{\partial}{\partial r_c}V_6(r_c) & \text{for} \quad \sigma < r < r_c \\ \infty & \text{for} \quad r < \sigma \\ 0 & \text{for} \quad r > r_c \end{cases} \tag{13}$$

$$V_6(r) = \epsilon(r - \sigma)^{-6}$$

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. In order to compensate any undesired effects by the above simplification, we do not really use the original cut-off r_c but increase the volume of the ellipsoid slightly. Thus we prevent the monomers to come too close without interacting.

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 detailled monomer mentioned above shows us 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.

Having fixed the geometric shape of the ellipsoid and defined a suitable potential we still have to determine the parameters σ and ϵ of the repulsive interaction (13). ϵ can be set to unity because we don't have an attractive part in our potential and therefore the determination of a "depth" makes no sense.

4 Summary

We have presented a parameterization of Bisphenol-A-Polycarbonate for the ellipsoid model. The ellipsoid model allows for simulating dense polymer systems at a coarse-grained level. 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.

5 Acknowledgements

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