# MODELLING OF Θ-CONDITIONS FOR BISPHENOL-A POLYCARBONATE SINGLE CHAINS

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Abstract: Assessing conformational dimensions of macromolecules is a topic of long-standing interest. Because of its simplicity, it is attractive to investigate the chain properties in Θ-conditions. Under these special conditions, the effects of excluded volume of the segments of the polymer chain vanish. The molecular chain is only subject to local constraints resulting from the bond structure and the hindrance to rotations about bonds. To model Θ-conditions a contour length dependent cutoff is introduced ensuring that only nonbonded interactions of atoms of neighbouring monomeric units are taken into account for energy calculations.
Using this energy model we will show that it is possible to model Θ-conditions of a single bisphenol-A polycarbonate (BPA-PC) chain in vacuum by two different methods: (i) (Pseudo-) Langevin dynamics simulations and (ii) regular reassignment of randomly generated atom velocities during a molecular dynamics simulation. Both methods can be used to avoid oscillative dynamic behaviour of the chain. Calculations of the end-to-end vector and the radius of gyration of the equilibrium ensembles derived from simulations at different temperatures show good agreement with experimental data. Thus our model techniques are well suited to simulate Θ-conditions with small computational expense.

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## INTRODUCTION

Investigation of the conformation of polymers is of great interest. In general the dependence of the spatial conformation is determined by short-range interactions and long-range interactions. The former are based on the local interactions between atoms and groups which are near neighbours. The latter are the interactions between chain units remote from one another in the chain sequence. These are nonbonded Coulomb and van der Waals interactions. Important features of a polymer are the unperturbed dimensions, which are the dimensions of the polymer in the Θ-state. The Θ-state is a reference state for experiment, theory and computer simulations. In the Θ-state the effects of excluded volume of the units of the polymer chain vanish. The polymer chain is only subject to local constraints resulting from the bond structure and the hindrance of rotations about bonds [1].

## REALISATION OF THE Θ-STATE

To model the Θ-state we introduced a contour length dependent cutoff $r_C$, ensuring that only nonbonded interactions of atoms in neighbouring monomeric units are taken into account for energy and gradient calculations. So we allow the chain to intersect itself, if the separation of the intersecting atoms is by more than two units or the spatial distance exceeds a predefined value $r_C$. This methodology was first suggested by Jung [2] and used by others [3,4].

The simulations were made with a BPA-PC single chain of 30 monomeric units in vacuum. Our beginning configuration is always a stretched one. In all simulations the time step is 1 fs and the cutoff is $r_C$=10 Å. For all calculation we use the parameters from the pcff forcefield [5-7]. The first step is a minimisation followed by the main MD simulation over several hundreds of picoseconds.

Due to the extended initial configuration the chain is under stress (at least entropically). This causes the formation of velocity components towards the centre of mass. As a result the chain coils up, penetrates itself and stretches again. Figure 1 shows an example of the time evolution of the end-to-end distance **r** and the radius of gyration **s**. Both oscillate in time with a period of about 100 ps. This behaviour is undesirable. We implemented two different methods to avoid

these oscillatory dynamics. They are (pseudo-) Langevin dynamics and TIBVR (Time Interval Based Velocity Reassignment) dynamics and are explained in the following sections.

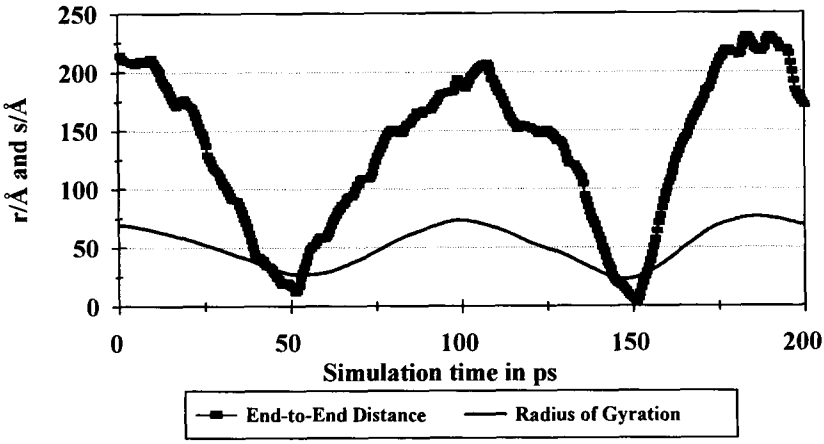


Figure 1 : Oscillatory behaviour of the end-to-end distance **r** and of the radius of gyration **s**. Simulation temperature is T=300 K.

## (PSEUDO-) LANGEVIN DYNAMICS

The Langevin equation of motion is [8] :

$$m\frac{d^2\vec{x}}{dt^2} = \vec{F}(t) - \varsigma\frac{d\vec{x}}{dt} + \vec{R}(t)$$

$m$ is the mass of the particle,

$\vec{x}$ are the coordinates of the particle,

$\vec{F}(t)$ is the systematic force,

$\vec{R}(t)$ is a random force with $\left\langle \vec{R}(t)\vec{R}(t')\right\rangle = 2\varsigma k_B T\delta(t-t')$,

$\varsigma = 4\pi\eta a$ is the friction constant

$\eta$ is the viscosity,

$a$ is the effective hydrodynamic radius.

Additionally to the modified nonbonded interactions the random force $\vec{R}(t)$ is explicitly implemented. The forces $\vec{R}(t)$ and $\varsigma d\vec{x}/dt$ have to be of the same magnitude. The parameter choice must ensure that the system is not going to be heated up or to be cooled down by the action of these two forces. Thus, the task of the velocity dependent force $\varsigma d\vec{x}/dt$ is to guarantee that the system is not cooled down or heated up as an effect of the random force. Instead of implementing this dissipative friction term explicitly, we apply the temperature control procedure of the MD algorithm. Thus we call it (pseudo-) Langevin dynamics. In the temperature control procedure a system temperature is calculated and compared with the target temperature. Then the velocity $v$ for every atom is rescaled every step according to the following relation:

$$\left(\frac{v_{New}}{v_{Old}}\right)^2 = \frac{T_{Target}}{T_{System}}$$

Thus the random force adds energy to the system, and the temperature control procedure dissipates energy. In balance the temperature does not drift.

The friction constant $\varsigma$ is an adjustable parameter of our (pseudo-) Langevin dynamics. $\varsigma$ includes further the effective hydrodynamic radius $a$ for each atom and the viscosity $\eta$. For simplicity we use $a$=0.7 Å for all atoms. For the adjustment of the viscosity $\eta$ there are two conditions to be fulfilled. The first is that the random force is strong enough to prevent the oscillatory behaviour of the chain. The second one is that the chain moves fast enough.

Table 1 : Effect of $\eta$ on the dynamics of the chain. Simulation temperature is T=300 K.

| **η/cPoise** | **Simulation time in ps** | **Dynamic behaviour** |
|---|---|---|
| 0.00000001 | 200 | Oscillative dynamic behaviour |
| 0.000001 | 200 | Oscillative dynamic behaviour |
| 0.0001 | 200 | Equilibrated |
| 0.0003 | 600 | Not equilibrated |
| 0.001 | 600 | Not equilibrated |
| 0.01 | 200 | Not equilibrated |

Table 1 shows the results of test runs with different viscosities. Calculation of the end-to-end distance **r** and radius of gyration **s** show the viscosity of $\eta$=0.0001 cPoise to be high enough to

prevent the oscillatory behaviour and to be small enough to allow the chain to equilibrate. Figure 2 demonstrates the evolution of the end-to-end distance **r** and the radius of gyration **s** during a (pseudo-) Langevin dynamics simulation.

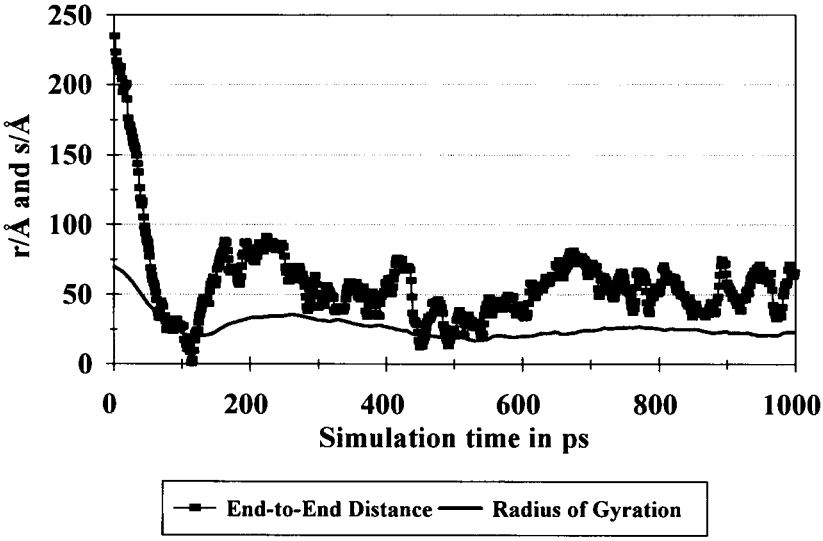


Figure 2 : Evolution of the end-to-end distance **r** and the radius of gyration **s** during a (pseudo-) Langevin dynamics simulation. The parameters are: T=400 K, $\eta$=0.0001 cPoise.

Both dimensions decrease rapidly towards the equilibrium value. Thus our choice for the parameter set used in (pseudo-) Langevin simulations is : $\eta$=0.0001 cPoise, $a$=0.7 Å and $r_C$=10 Å.

The results of various (pseudo-) Langevin dynamics simulations at different temperatures are shown in Figure 3 and Figure 4. Each dynamic run is taken over 1000 ps. After equilibration (200 ps) the runs are split into four subruns each 200 ps long. These subruns are taken to be independent. For each subrun $\langle \mathbf{r}^2 \rangle / M$ and $\langle \mathbf{s}^2 \rangle / M$ are calculated . The values in Figure 3 and Figure 4 are means and the error bars are standard deviations of these values. In general $\langle \mathbf{r}^2 \rangle / M$ is between 0.3 and 0.6 Å$^2$, and $\langle \mathbf{s}^2 \rangle / M$ is between 0.07 and 0.12 Å$^2$.

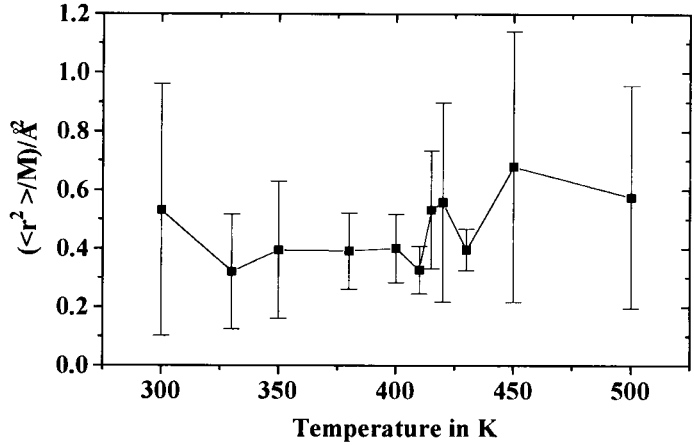


Figure 3 : Mean-square end-to-end distance $\langle r^2 \rangle / M$ of (pseudo-) Langevin dynamics simulations.

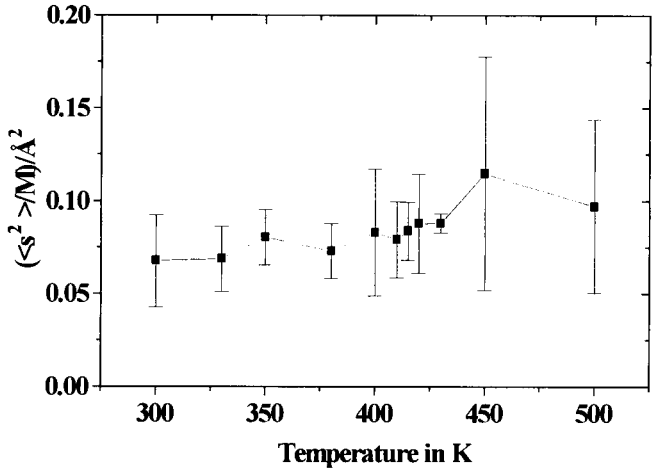


Figure 4: Mean-square radius of gyration $\langle s^2 \rangle / M$ of (pseudo-) Langevin dynamics simulation.

TIBVR DYNAMICS

Time interval based velocity reassignment (TIBVR) dynamics is also used to avoid the undesired oscillatory behaviour of the chain. As pointed out above the origin of this behaviour is the formation of velocity components towards the centre of mass. The idea is to reassign the velocities due to a Boltzmann distribution after a specific time $\tau_S$, and thus to destroy the undesired velocity components. The time interval $\tau_S$ is a new parameter of the simulations. If $\tau_S$ is too short compared to the period of the oscillation, then the dynamics would be determined by the procedure of assigning the Boltzmann distributed velocities. On the other hand, the more we increase $\tau_S$ the less is the effect of the reassignment. The period of the oscillation is approximately 100 ps (see Figure 1). For $\tau_S$ we use approximately a third of this period, i.e. $\tau_S$=30 ps. Thus the parameters of the second method are a contour length dependent cutoff, $r_C$=10 Å, and a velocity reassignment period, $\tau_S$=30 ps. Due to the random character of the velocity reassignment the system may take more than 200 ps to equilibrate. Thus the simulations are taken over 1200 ps. An example of the time evolution of the end-to-end distance **r** and the radius of gyration **s** during a TIBVR run is shown in Figure 5. Both **r** and **s** decrease to their equilibrium values within 200 ps.

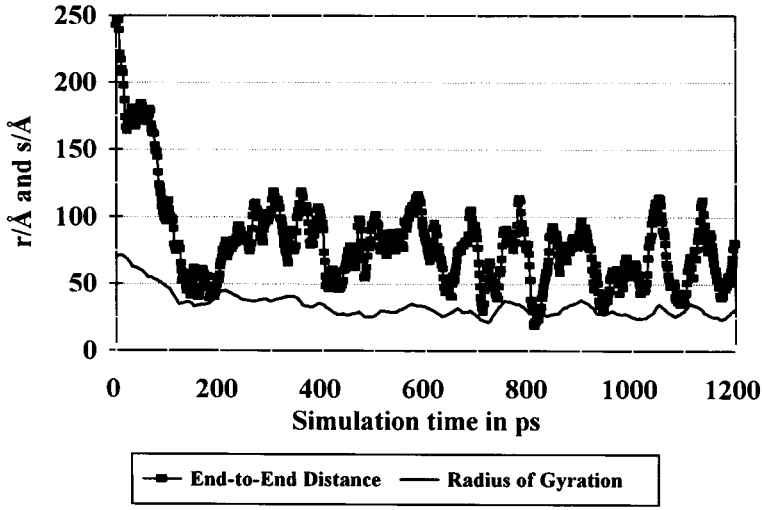


Figure 5: Evolution of the end-to-end distance **r** and the radius of gyration **s** during a TIBVR dynamics run. Simulation temperature is T=400 K.

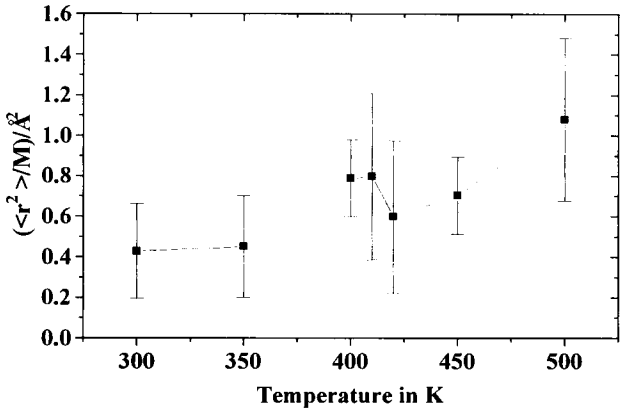


Figure 6: Mean-square end-to-end distance $<\mathbf{r}^2>/M$ of TIBVR dynamics simulations.

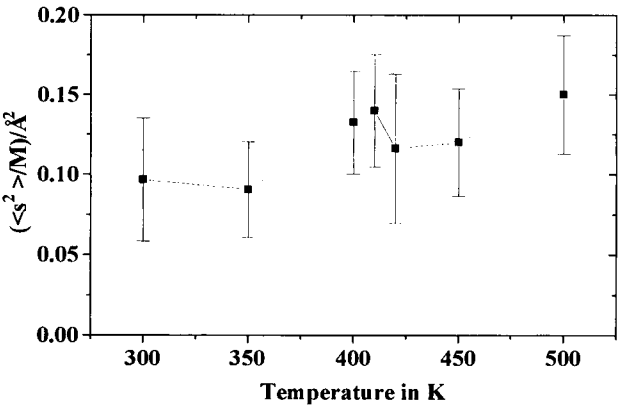


Figure 7: Mean-square radius of gyration $<\mathbf{s}^2>/M$ of TIBVR dynamics simulations.

For the calculation of $<\mathbf{r}^2>/M$ and $<\mathbf{s}^2>/M$ of each run, only the remaining time after equilibration is taken into account that varies for different simulations. This time is then divided into four subruns. These are taken to be independent. For each of them $<\mathbf{r}^2>/M$ and $<\mathbf{s}^2>/M$ as well as their mean and the standard deviation are calculated. They are shown in Figure 6 and

Figure 7 for different temperatures. The values for $\langle r^2 \rangle / M$ are between 0.4 and 1.2 Å$^2$, and those for $\langle s^2 \rangle / M$ are between 0.09 and 0.15 Å$^2$.

## CONCLUSION

We present two different methods, (pseudo-) Langevin dynamics simulations and TIBVR simulations for modelling Θ-conditions on a BPA-PC single chain in vacuum. The reference values for the Θ-state reported in the *Polymer Handbook* [9] are $0.70 < (\langle r^2 \rangle / M)/Å^2 < 0.88$. According to the relation $\langle s^2 \rangle / M = \langle r^2 \rangle / (6M)$ we obtain $0.12 < (\langle s^2 \rangle / M)/Å^2 < 0.15$. There are other reported values of $0.13 < (\langle s^2 \rangle / M)/ Å^2 < 0.21$ [11-13]. Taking into account that our chain is small (M = 7630) compared to those used in experiments with M >100000, our results are in fair agreement with experimental data. Thus both of our modelling techniques are suited to simulate Θ-conditions with small computational expense.

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