Polymer 51 (2010) 4008–4014

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Relaxation of amorphous multichain polymer systems using inverse kinematics

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ARTICLE INFO

Article history:
Received 19 May 2010
Received in revised form
7 June 2010
Accepted 7 June 2010
Available online 25 June 2010

Keywords:
Amorphous polymers
Inverse kinematics
Rebridging scheme

ABSTRACT

Atomic scale simulations of polymer materials is a topic of interest since it permits to reduce costly experiments to determine their physicochemical properties. In this context, modeling heterogeneously ordered multichain systems such as amorphous polymers, remains a challenging problem. A recently proposed two-step method consists of iteratively generating the structures using a simplified energy model, and subsequently relaxing the system, considering a more accurate model, in order to reduce its potential energy. This work proposes an improvement of this method by integrating a novel relaxation technique, which applies analytical rebridging moves inspired by robotics. A comparative analysis using models of amorphous polyethylene with different sizes and densities shows that the rebridging scheme described here is very effective for the simulation of long alkanes.

1. Introduction

The development of simple theoretical strategies to model and study many fundamental problems of complex soft matter by means of computer simulations is a topic of growing interest within Polymer Physics [1–5]. Within this field, conventional atomistic Molecular Dynamics (MD) and Monte Carlo (MC) simulations based on force-field potentials are very useful to describe the behavior of medium- and long-polymer chains in solution. Nevertheless, it is well known that the application of these simulation techniques to heterogeneously ordered multichain systems, e.g. amorphous polymers, is very unpractical because the high density and the connectivity of the molecular chains in macromolecular systems reduce significantly the efficiency of these algorithms [6]. In order to overcome these difficulties, many approaches have appeared in the literature. The simplest ones consist on energy minimization of microstructures that are generated randomly [7] or using chain growth techniques based on rotational isomeric states [8]. However, in recent years more sophisticated procedures have been reported. In our opinion, among the most remarkable are those based on the generation of structures of low density, which are slowly compressed until the desired density is reached [9,10], the geometric optimization using heuristic search algorithms [11,12], the construction of polymer chains by polymerization of monomers previously equilibrated in a simulation box [13], the construction of high coordination lattices [14,15], and the application of advanced chain-connectivity altering algorithms like end-bridging [16,17], directed end-bridging [18] and double-bridging [19,20]. In recent works, we reported an alternative strategy, denoted SuSi (Structure Simulation), for generating microstructures of amorphous polymers avoiding atomic overlaps and obeying the proper torsional distribution. The method is based on a two-step strategy. First, atomistic models are generated atom-by-atom using an algorithm that minimizes the energy associated with the torsional degrees of freedom [21,22]. After this, the non-bonding interactions of the generated structures are relaxed. Three different relaxation algorithms were implemented and tested. The simplest one corresponds to a typical minimization algorithm, which was found to be ineffective [21]. The second relaxation algorithm was derived from the geometric aspects of the Configuration Bias (CB) MC method [23]. In this procedure, a randomly selected polymer chain is cut at an arbitrary position and, sequentially, rebuild bond-by-bond [24–26]. For each bond to be appended a set of K torsional angles is randomly chosen between 0 and 2π, the energy associated to each of the K positions being evaluated. One of the positions is randomly chosen with probability proportional to its Botzmann weight. Although this relaxation algorithm was found to be very effective

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doi:10.1016/j.polymer.2010.06.019

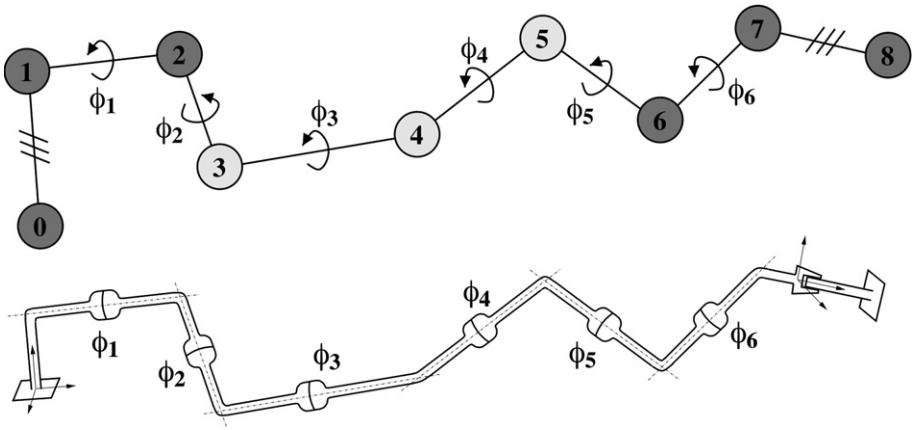

Fig. 1. A molecular chain of 9 bonded atoms (top) can be seen as a 6R robotic manipulator (bottom). The bond torsions correspond with the joint angles. Fixing the three first and the three last atoms of the molecular chain is analogous to fixing the base and the end-effector of the manipulator.

for the modeling of systems bearing complex architectures, *e.g.* comblike polymers [27,28], it was not very useful for linear molecules because of the difficulties to relax the interior segments of chain molecules [23]. The third relaxation procedure was based on the geometric aspects of the Concerted Rotation (ConRot) method [23,29,30]. In this advanced MC procedure, a chain is selected at random and interrupted at an arbitrary position, *i*, by deleting the next *L* consecutive atoms of the main chain. Then, the ConRot geometric algorithm joins the two segments of the interrupted polymer chain rebuilding the positions for the *L* deleted atoms. This relaxation algorithm was successfully used to study the properties of polymers with conventional architectures, *e.g.* linear polyethylene (PE), in the amorphous state [23,31].

In this work, we propose an improved MC-like algorithm for the relaxation of linear amorphous polymers, which is shown to be significantly more effective than the previous method based on ConRot. More specifically, we have implemented a geometric trimer rebridging method inspired by robotics. The molecular chain is modeled as an articulated mechanism, and then, an *inverse kinematics* (IK) method is applied to generate moves that satisfy geometric constraints. A similar approach was proposed by Wu and Deem [32] for the theoretical study of the *cis/trans* isomerization of proline-containing cyclic peptides. More generally, the application of robot kinematics methods to solve problems related with molecular modeling has lead to effective techniques for protein loop modeling, or for the conformational analysis of cyclic molecule [33–39]. However, to the best of our knowledge, such methods have not yet been used to study dense multichain macromolecular systems. The work is organized as follows. Next section provides a detailed description of the intramolecular rebridging relaxation method inspired by robotics. Next, the geometric ConRot strategy is briefly reminded. The performance of the two relaxation methods is then evaluated and compared using amorphous PE as test system. Several tests are carried out to analyze the influence of the size of the system, the number of chains, and the density on the efficiency of the two methods. It should be emphasized that amorphous PE is a very well-known system, whose properties have been extensively investigated using very different simulation methods. Accordingly, we mainly focused on the efficiency of the IK and geometric ConRot procedures, analyses of the PE relaxed microstructures being reduced to a few structural parameters. Finally, the conclusions are outlined and some possible extensions of this work are proposed.

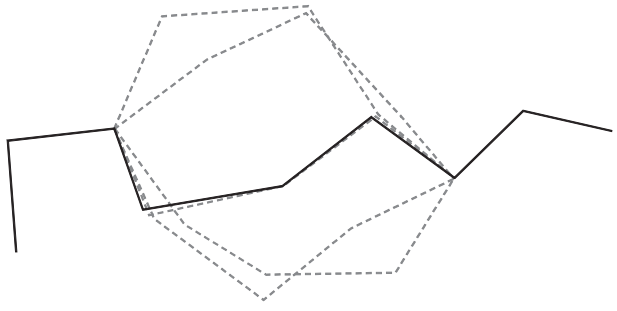

Fig. 2. Six solutions for the trimer rebridging problem in Fig. 1: the original conformation (plain line), and five alternative ones (dashed lines).

2. Intramolecular rebridging by inverse kinematics

This section describes a geometric trimer rebridging method inspired by robotics. The idea is illustrated in Fig. 1. Next subsection formulates the trimer rebridging problem, making an analogy between a molecular chain and an articulated mechanism. Then, the adopted solution method is described, and the particular application in the context of polymer relaxation is explained.

2.1. Problem formulation

Consider a molecular chain segment formed by 9 consecutively bonded atoms, in which bond lengths and bond angles are kept fixed at their equilibrium values, *i.e.* dihedral angles are the only degrees of freedom. If the first three atoms {0,1,2} and the last three ones {6,7,8} are kept fixed at their positions, the six dihedral angles (ϕ_1–ϕ_6) only accept sets of values able to satisfy this geometric constraint. Obviously, the positions allowed for the three atoms in the middle {3,4,5} are univocally determined by the values of the dihedral angles. According to these considerations, the trimer rebridging problem consists in finding the admissible values of the six dihedral angles.

In order to solve this problem, an analogy is proposed between a molecular chain in which the dihedral angles are the only degrees of freedom and an articulated mechanism composed of rigid bodies connected by revolute joints, such as a robotic manipulator. According to this, the trimer rebridging problem is analogous to the IK problem for a six revolute (6R) jointed manipulator: obtain the values of the 6 revolute joints that satisfy a given pose of the end-effector with respect to the base. From the seventies, this problem has deserved much attention within the robot kinematics community, effective solutions being currently available for particular geometries, *i.e.* particular relative locations of consecutive joints, as well as for the general case. In general, the