



Relaxation of amorphous multichain polymer systems using inverse kinematics

Juan Cortés^{a,b,**}, Sergio Carrión^c, David Curcó^d, Marc Renaud^{a,b}, Carlos Alemán^{c,e,*}

^a CNRS, LAAS, 7 avenue du colonel Roche, F-31077 Toulouse, France

^b Université de Toulouse, UPS, INSA, INP, ISAE, LAAS, F-31077 Toulouse, France

^c Departament d'Enginyeria Química, E. T. S. d'Enginyers Industrials, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

^d Departament d'Enginyeria Química, Facultat de Química, Universitat de Barcelona, Martí Franques 1, Barcelona E-08028, Spain

^e Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona E-08028, Spain

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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.

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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 Boltzmann weight. Although this relaxation algorithm was found to be very effective

* Corresponding author at: Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona E-08028, Spain.

** Corresponding author at: CNRS, LAAS, 7 avenue du colonel Roche, F-31077 Toulouse, France.

E-mail addresses: jcortes@laas.fr (J. Cortés), carlos.aleman@upc.edu (C. Alemán).

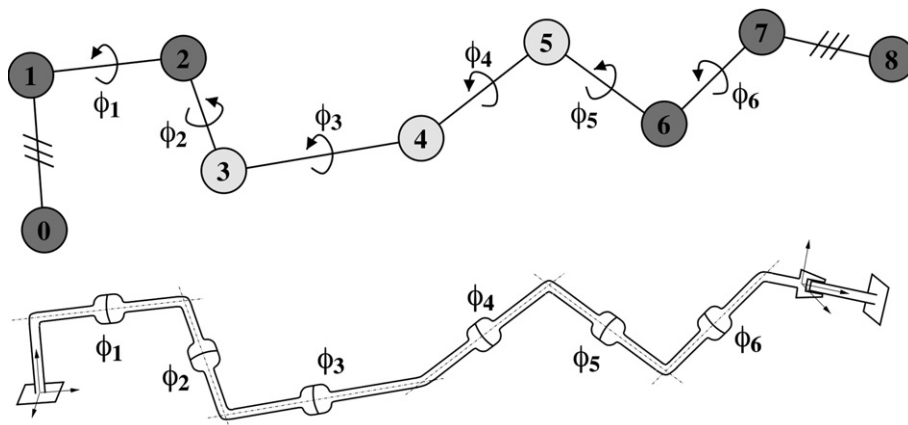


Fig. 1. A molecular chain of 9 bonded atoms (top) can be seen as a 6R robotic manipulator (bottom). The bond torsions correspond with the joint angles. Fixing the three first and the three last atoms of the molecular chain is analogous to fixing the base and the end-effector of the manipulator.

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.

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

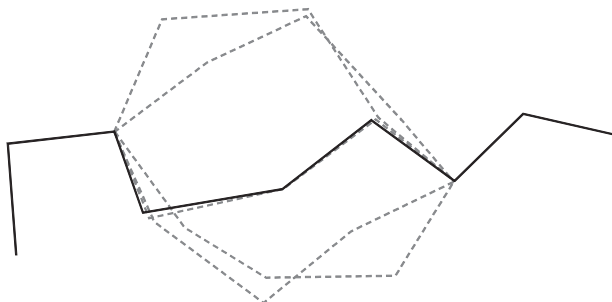


Fig. 2. Six solutions for the trimer rebridging problem in Fig. 1: the original conformation (plain line), and five alternative ones (dashed lines).

Table 1

Efficiency (EF; in %) of the 6R IK and geometric ConRot relaxation methods for the multichain polyethylene (PE) systems tested in this work. EF is defined as the average reduction (in %) of the energy, with respect to the generated microstructures, after the application of a given number relaxation steps. For each PE system the number of chains (N), the number of atoms per chain (M) and the density (ρ) are indicated.

{N, M}	ρ (g cm ⁻³)	Geometric ConRot			6R IK
		1000 steps	5000 steps	10000 steps	1000 steps
4, 400 ^a	0.85	8	25	36	43
2, 200 ^b	0.85	23	47	55	70
4, 200 ^b	0.85	14	36	45	57
8, 400 ^b	0.85	4	16	25	28
8, 800 ^b	0.85	2	10	16	17
4, 400 ^b	1.00	7	22	31	39
4, 400 ^b	1.10	6	20	28	35
4, 400 ^b	1.20	5	18	23	31

^a EF values calculated considering 1000 and 50 PE microstructures were identical.

^b EF was calculated considering 50 microstructures.

6R IK problem has a finite number of solutions, with an upper bound of 16 [40]. Fig. 2 represents the solutions to the problem illustrated in Fig. 1.

2.2. 6R IK solver

The method applied in this work for solving the 6R IK problem has been adapted from the general solver proposed by Renaud [41,42]. This solver is based on algebraic elimination theory, and develops an *ad-hoc* resultant formulation inspired by the work of Lie and Liang [40]. Starting from a system of equations representing the IK problem (the formulation involves the product of homogeneous transformation matrices), the elimination procedure leads to an 8×8 quadratic polynomial matrix in one variable. The problem can then be treated as a generalized eigenvalue problem, as was previously proposed by Manocha and Canny [43], for which efficient and robust solutions are available [44] (our implementation uses the LAPACK routine DGGEV [45]). Technical details on the applied IK solver are provided in the report of Renaud [46].

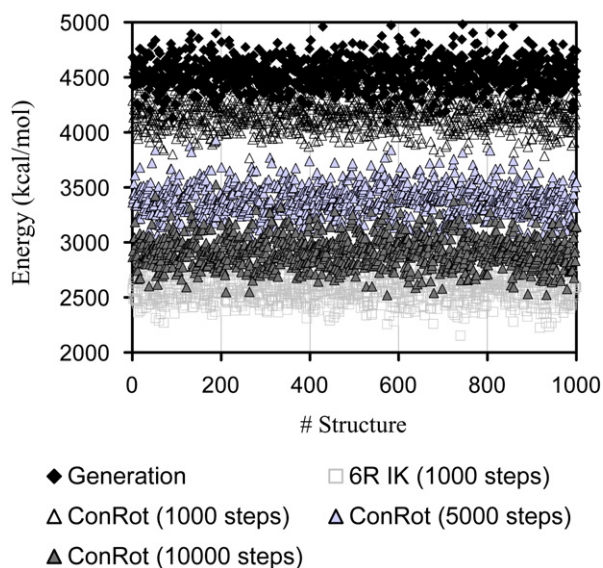


Fig. 3. Comparison between the energies resulting from the generation algorithm, the energies obtained after 1000 steps of 6R IK relaxation, and the energies obtained after 1000, 5000 and 10,000 steps of geometric ConRot relaxation for a set of 1000 PE microstructures constituted by 4 chains and 400 pseudoparticles per chain ($\rho = 0.85$ g cm⁻³).

The overall code of the 6R IK solver, programmed in language C/C++, has been optimized to achieve very fast computation. Solutions are computed in 0.4 ms on a single processor (tests were performed on a single core of a 2.4 GHz Intel Core Duo processor). It should be noted that a variant of this method has been successfully applied to model long protein loops [35].

2.3. Application to heterogeneously ordered multichain polymeric systems

The 6R IK solver has been adapted to generate intermolecular rebridging moves applying similar conditions to those used for the geometric ConRot algorithm in our previous work (see below) [23]. Thus, a random perturbation of a few degrees is applied to the dihedral angle preceding ϕ_1 , *i.e.* the dihedral angles that defines the rotation around the bond formed by atoms 0 and 1 in Fig. 1. Then, the 6R IK solver computes the new conformations of the trimer able to satisfy the geometric constraints of the molecular chain. Since microscopic reversibility is not required in the framework of relaxation, all the solutions provided by the solver are feasible moves. Note that the computing time needed for the solver to obtain a single solution (the one corresponding to a continuous motion produced by the perturbation) is approximately the same as that required for obtaining all the solutions.

3. Geometric ConRot

Consider a randomly selected atom, *e.g.* atom 2 in Fig. 1, within a molecular chain, the L consecutive atoms are deleted (in this work $L = 4$). The procedure used to rebuild the positions of the deleted atoms can be summarized in the following two steps: (i) the dihedral angle formed by atoms {0,1,2}, whose coordinates remain fixed, and the first deleted atom {3}, that is ϕ_1 , is changed by adding a random perturbation of a few degrees; and (ii) the position of the other three deleted atoms {4,5,6} is determined by numerically solving a system of equations involving constant values of bond lengths and bond angles imposed by the fixed geometry of the chain. Thus, only one of the seven dihedral angles involved in a move with $L = 4$ is considered as an independent variable, with the rest being imposed by the internal geometry of the system. According to this, the geometric ConRot and the intramolecular rebridging by IK strategies essentially differ in the solver: the former uses a numerical procedure [29], while the latter applies an analytical method [42]. Finally note that, in average, the CPU time required to solve the geometric trimer rebridging problem with our implementation of ConRot is 1.3 ms.

4. Test calculations

4.1. Simulated systems and force-field

Systems formed by N PE chains, each one containing M CH₂ pseudoatoms (CH₃ at chain ends) connected by rigid bond lengths (1.526 Å) and angles (112.4°), have been used to compare the efficiency of the 6R IK and the geometric ConRot relaxation methods. Specifically, the PE microstructures considered in this work were defined by the following { N,M } values: {2200}, {4200}, {4400}, {4600}, {4800} and {8800}.

The intramolecular interactions between two pseudoatoms separated by more than four bonds and all the intermolecular interactions, *i.e.* non-bonding interactions, have been represented by a pairwise additive Lennard-Jones 12–6 potential:

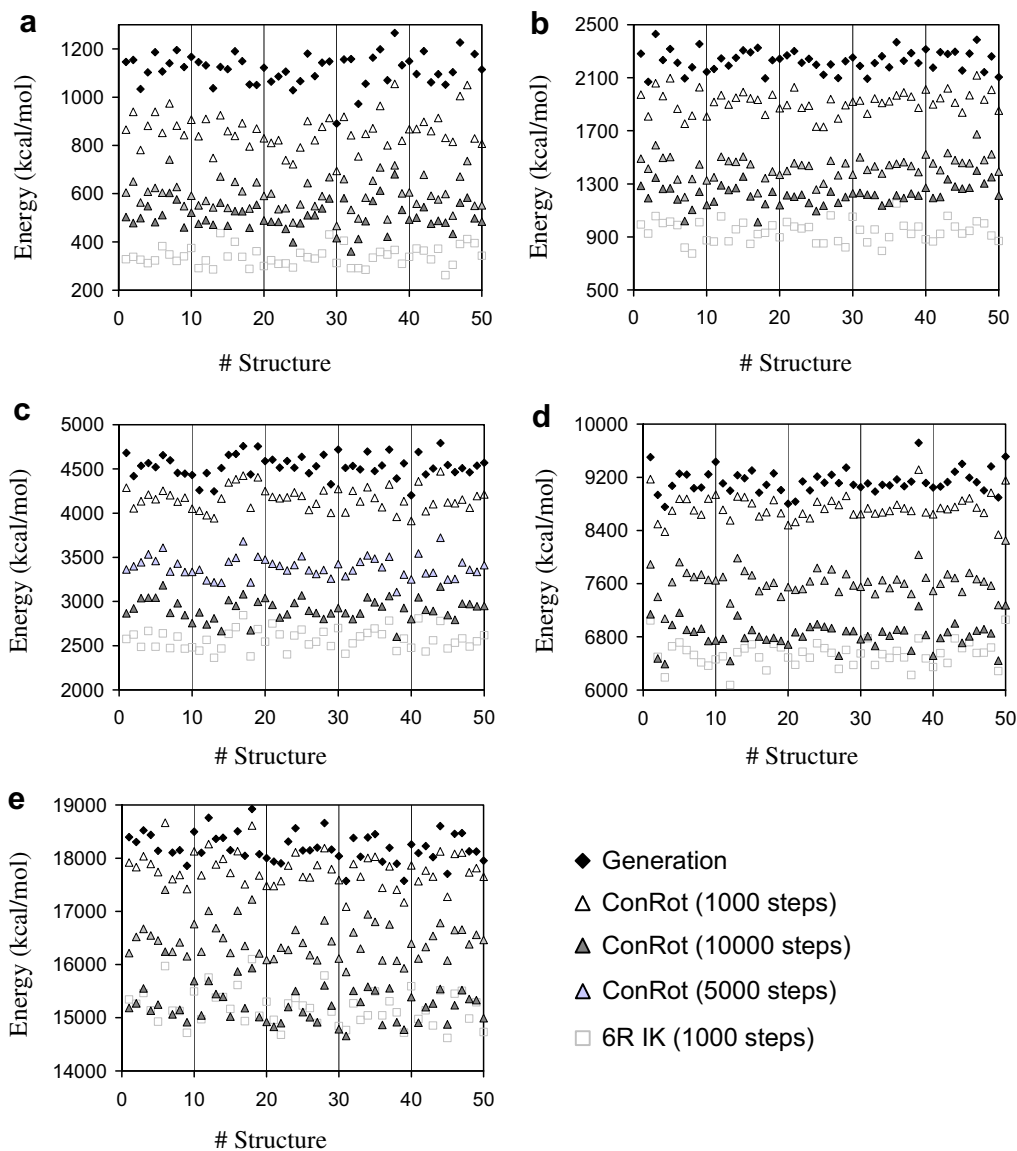


Fig. 4. Comparison between the energies resulting from the generation algorithm, the energies obtained after 1000, 5000 and 10,000 steps of geometric ConRot relaxation for a set of 50 PE microstructures constituted by N chains and M pseudoparticles per chain, $\{N,M\}$, at $\rho = 0.85 \text{ g cm}^{-3}$: (a) {2200}; (b) {4200}; (c) {4400}; (d) {8400}; and (e) {8800}.

$$E_{ij} = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \quad (1)$$

where $A_{ij} = \varepsilon_{ij}R_{ij}^{12}$, $B_{ij} = 2\varepsilon_{ij}R_{ij}^6$, $\varepsilon_{ij} = \varepsilon_i\varepsilon_j$ and $R_{ij} = R_i + R_j$. The van der Waals parameters (ε_i and R_i) of CH_2 and CH_3 pseudoatoms have been taken from the Amber force-field: [45] $\varepsilon(\text{CH}_2) = 0.12 \text{ kcal/mol}$, $\varepsilon(\text{CH}_3) = 0.15 \text{ kcal/mol}$, $R(\text{CH}_2) = 1.925 \text{ \AA}$ and $R(\text{CH}_3) = 2.000 \text{ \AA}$. On the other hand, the dihedral angle interactions have been described using the following torsional potential:

$$E_\phi = \sum_{n=1}^3 \frac{V_n}{2} (1 + \cos(n\phi - \gamma_n)) \quad (2)$$

where V_n is a force constant, n is the multiplicity factor and γ_n is phase angle. The torsion around the $\text{CH}_2\text{--CH}_2$ and $\text{CH}_2\text{--CH}_3$ bonds have been represented using the following parameters: $V_3 = 2.0 \text{ kcal/mol}$ and $\gamma_n = 0^\circ$. A scale factor of 0.5 has been applied to reduce all the non-bonding interactions within atoms of the

same chain separated by exactly three bonds (1–4 interactions). The scaling of the 1–4 interactions is consistent with the analytical energy expression showed above and the potential energy parameters of the Amber force-field [46].

4.2. Generation of microstructures

Representative microstructures of amorphous PE defined by $\{N, M\} = \{2200\}, \{4200\}, \{4400\}, \{4800\}$ and $\{8800\}$ were generated at the experimentally observed density ($\rho = 0.85 \text{ g cm}^{-3}$) using a previously reported algorithm [21,22], which is briefly reminded below. In addition, {4400} multichain PE microstructures were generated at higher densities ($\rho = 1.00, 1.10$ and 1.20 g cm^{-3}).

The generation method packs polymer chains in a box of given dimension, i.e. at a given density, inducing minimum torsional strain, which is achieved by multiplying the radii R_i by a scale factor λ . The coordinates of the NM atoms of radii $\{\lambda \cdot R_i\}$ are generated atom-by-atom and chain-by-chain according to the following procedure: (i)

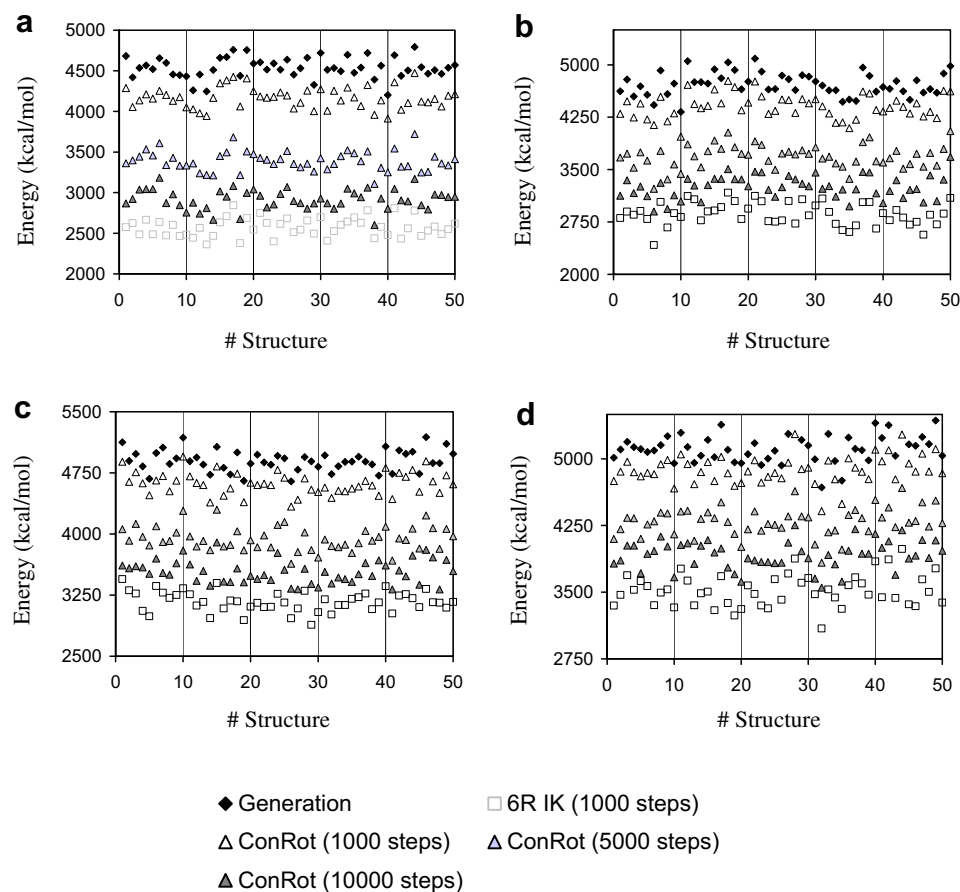


Fig. 5. Comparison between the energies resulting from the generation algorithm, the energies obtained after 1000 steps of 6R IK relaxation, and the energies obtained after 1000, 5000 and 10,000 steps of geometric ConRot relaxation for a set of 1000 PE microstructures constituted by 4 chains and 400 pseudoparticles per chain, {4400}, at $\rho = 0.85$ (a), 1.00 (b), 1.10 (b) and 1.20 g cm^{-3} (d).

three bonded atoms of the first chain are placed at arbitrary positions within the simulation box; (ii) a number, k , of positions are randomly generated for the fourth atom and the energy associated to every position, $\{E_j, j = 1, \dots, k\}$, is calculated. One position is chosen through a typical Metropolis MC acceptance criterion; (iii) k positions are generated for the fifth atom, which are categorized as *unfeasible* or *feasible* depending if atomic overlaps with the atoms previously generated and separated by more than three bonds exist or not, respectively. The energy of the j *feasible* positions ($j \leq k$) is used in the Metropolis criterion mentioned above to select one, while the *unfeasible* positions are discarded. This point is repeated for the remaining atoms of the chain; (iv) the coordinates of the M atoms of the next chains are generated using the same strategy. The only difference affects the positions of the first three atoms, which are found using a random search procedure to avoid steric clashes with the atoms belonging to chains created previously.

It should be emphasized that the energy of the generated positions, E_j , is in all cases evaluated as the sum of the torsional and van der Waals contributions associated with the particles separated from j by three chemical bonds (1–4 interactions). The omission of interactions different from 1 to 4 notably reduces the CPU effort, whereas, at the same time, a minimum torsional strain for the generated chain is guaranteed. Obviously, the van der Waals energies are calculated using the unscaled atomic radii R_i , the scaled radii being exclusively used to examine the overlapping between the atoms at the k generated positions. All the structures generated in this work were obtained using $\lambda = 0.69$, which was found to provide good results for amorphous PE [22].

4.3. Comparison of the two relaxation methods

The efficiency of a relaxation method (EF) is defined as the average reduction (in%) of the energy, with respect to the generated microstructures, after the application of a given number relaxation steps. Table 1 lists the EF for all the PE systems considered in this work.

Initially, the performance of the intramolecular rebridging by IK and the geometric ConRot was compared by considering the {4400} PE ($\rho = 0.85 \text{ g cm}^{-3}$). Fig. 3 shows, for a set of 1000 representative structures: the energies of the generated structures, the energies obtained after 1000 steps of 6R IK relaxation, and the energies achieved after applying 1000, 5000 and 10,000 steps of geometric ConRot. As it can be seen, the latter method needs a relatively large number of steps to achieve a significant reduction in the energy. Thus, after 1000, 5000 and 10,000 steps of relaxation, the energy of the generated microstructures decreases in average by 8%, 25% and 36%. In contrast, the EF amounts to 43% after applying only 1000 steps of 6R IK. Accordingly, the later relaxation algorithm is not only faster but also significantly more efficient than the geometric ConRot for medium size heterogeneously ordered multichain systems.

Fig. 4 analyzes the influence of the size of the chains and the number of chains in the efficacy of the two relaxation algorithms by comparing the energies of 50 microstructures generated for {2200}, {4200}, {4400} and {8400} and {8800} systems ($\rho = 0.85 \text{ g cm}^{-3}$ in all cases) before and after relaxation. As it was expected, the EF provided for the {4400} system (Fig. 4c) is identical to that

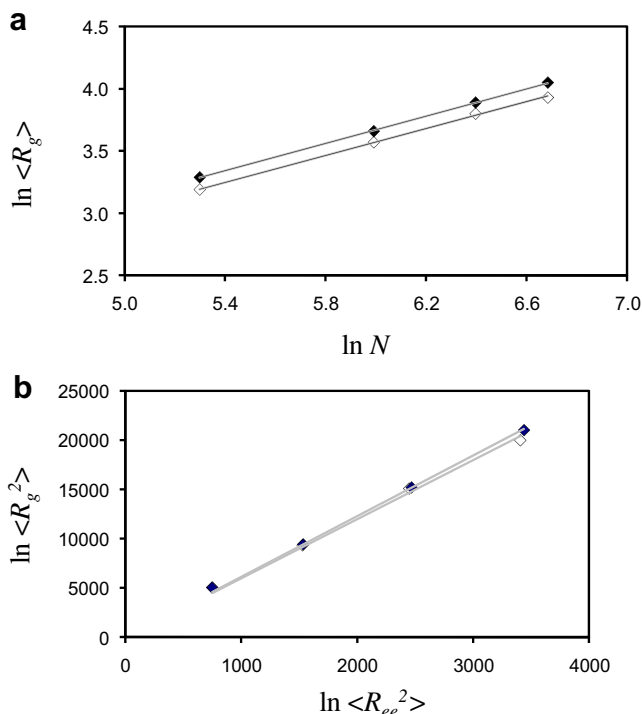


Fig. 6. Plots of (a) $\ln \langle R_g \rangle$ as a function of $\ln N$ and (b) $\langle R_g^2 \rangle$ against $\langle R_{ee}^2 \rangle$ for the PE microstructures relaxed using the 6R IK (black diamonds) and geometric ConRot (white diamonds) algorithms. The solid gray lines correspond to the linear regressions (a) $y = ax + b$ and (b) $y = cx$.

displayed in Fig. 3 for a set of 1000 independent microstructures, *i.e.* the energy decreases 43% and 36% after 1000 steps of 6R IK and 10,000 steps of geometric ConRot respectively, indicating that results obtained for 50 microstructures are statistically representative. The EF of the 6R IK (Table 1) increases to 70% and 57% for the {2200} and {4200} systems, respectively, while decreases to 28% and 17% for {8400} and {8800} systems. These results clearly reflect that this relaxation method becomes less efficient when the number of pseudoatoms contained in the system increases through the size of the individual molecules and/or the number of chains. On the other hand, the energy reduction achieved after apply 10,000 steps of geometric ConRot on the same PE microstructures generated for the {2200}, {4200}, {8400} and {8800} systems amounts to 55%, 45%, 25% and 16%, respectively, revealing a very similar behavior. Indeed, Fig. 4e clearly shows that the degree of relaxation reached by the two methods is very close for the largest system. In spite of this, it should be emphasized that the efficiency of the 6R IK solver is significantly higher than that of the geometric ConRot, since the number of steps required for similar energy reductions differ in one order of magnitude.

The influence of the density on the efficiency of the two relaxation methods has been examined by considering 50 PE microstructures generated considering the {4400} system at $\rho = 0.85, 1.00, 1.10$ and 1.20 g cm^{-3} . The variation of the energy upon relaxation is displayed in Fig. 5. As it can be seen in Table 1, after 1000 steps of 6R IK the EF decreases from 43% to 31% when the ρ increases from 0.85 to 1.20 g cm^{-3} , while the evolution of the EF reached upon 10,000 steps of geometric ConRot drops from 36% to 23%. Thus, although the 6R IK was the most efficient method in all cases, the relative variation of the EF with the density was similar for the two relaxation procedures.

The reliability of the PE structures relaxed using the 6R IK solver and the geometric ConRot algorithm has been investigated by

analyzing the radius of gyration (R_g) and the end-to-end distance (R_{ee}). The R_g of PE is well described by:

$$R_g = bN^v \quad (3)$$

where N is number of CH₂ groups (N) and v is an universal coefficient close to 0.5. A coefficient $v = 0.50$ has been predicted by ideal RIS chains, while numerous computer simulations using atomistic and coarse-graining models have provided v values ranging from 0.52 to 0.59 [47–49]. Fig. 6a represents $\ln \langle R_g \rangle$ as a function of $\ln N$ for {4200}, {4400}, {4600} and {4800} relaxed PE microstructures ($\rho = 0.85 \text{ g cm}^{-3}$), where the bracket refers to the average overall conformations. As can be seen, $\ln \langle R_g \rangle$ depends linearly on $\ln N$, the correlation coefficients derived from the fittings being $R^2 = 0.999$ in all cases. The parameter v deduced for the microstructures relaxed using the IK and geometric ConRot methods is 0.548 ± 0.012 and 0.539 ± 0.009 , respectively. Thus, taking into account the statistical errors associated to simulation results, it can be stated that the two slopes are equal (Fig. 6a).

On the other hand, R_{ee} and R_g are related by:

$$\langle R_{ee}^2 \rangle = 6 \langle R_g^2 \rangle \quad (4)$$

Fig. 6b represents $\langle R_g^2 \rangle$ against $\langle R_{ee}^2 \rangle$ for the {4200}, {4400}, {4600} and {4800} relaxed PE microstructures. The linear regressions of the two sets of points, $\langle R_{ee}^2 \rangle = c \cdot \langle R_g^2 \rangle$, provided the following coefficients: $c = 6.14 \pm 0.14$ (6 K IR solver) and 6.00 ± 0.22 (geometric ConRot), the regression coefficients being $R^2 > 0.99$. Notice that an excellent agreement with the ideal behavior displayed in Eqn. (4) was obtained in the two cases.

5. Conclusions

A new efficient procedure originating from robotics has been proposed to relax microstructures of heterogeneously ordered multichain systems in which the dihedral angles are the only degrees of freedom. Within this method, a molecular chain is modeled as an articulated mechanism, and moves that satisfy geometric constraints are analytically obtained using a 6R IK solver. This relaxation method results particularly useful when it is combined with a good generation algorithm. Thus, such combination permits to obtain independent representative microstructures of amorphous polymers with minimal computational resources. The efficiency of the proposed IK method has been compared with that of the geometric ConRot, which was found to be a very powerful numerical method derived from advanced MC strategies. Test calculations using PE microstructures (polybeads) considering variation in the number of polymer chains, size of the chains and density show that the relaxation method using 6R IK is significantly more efficient and faster than the one using the geometric ConRot.

The results presented in this paper only involve the aforementioned local moves generated by perturbing one dihedral angle. Nevertheless, other types of moves can also be generated using the proposed approach. For instance, the bond torsion following ϕ_6 , *i.e.* the torsion of the bond between atoms 7 and 8 in Fig. 1, could also be perturbed. Besides, perturbations of bond lengths and bond angles in the considered 9-atom segment could also be introduced before applying the 6R IK solver. Another possible extension will be the application of the 6R IK solver to generate moves involving non-consecutive bond torsions. This is feasible because the solver does not require consecutive revolute joint axes to be co-punctual, *i.e.* 6 dihedral angles could be arbitrarily chosen within the whole macromolecular chain.

Finally, mention that the proposed rebridging moves are fully compatible with other types of moves such as chain-connectivity altering moves (*e.g.* end-bridging), which are able to better

equilibrate long-length-scale conformational properties of polymers. Indeed, a very effective relaxation method for general polymer systems should be obtained by a suitable combination of moves.

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References

- [1] Bachnagel J, Binder K, Doruker P, Gusev AA, Hahn O, Kremer K, et al. *Adv Polym Sci* 2000;152:41.
- [2] Kremer K. *Macromol Chem Phys* 2003;204:257.
- [3] Everaers R, Sukumaran SK, Grest GS, Svaneborg C, Sivasubramanian A, Kremer K. *Science* 2004;303:823.
- [4] Theodorou DN. *Comput Phys Commun* 2005;169:82.
- [5] Alemán C, Karayiannis NCh, Curcó D, Foteinopoulou K, Laso M. *J Mol Struct (Theochem)* 2009;898:62.
- [6] Leontidis E, Forrest B, Widmann AH, Suter UW. *J Chem Soc Faraday Trans* 1995;91:2355.
- [7] Theodorou DN, Suter UW. *Macromolecules* 1985;18:1467.
- [8] Rapold RF, Suter UW. *Macromol Theory Simul* 1994;3:1.
- [9] McKechnie JI, Brown D, Clarke JHR. *Macromolecules* 1992;25:1562.
- [10] Gusev AA, Zehnder MM, Suter UW. *Macromolecules* 1994;27:615.
- [11] Müller M, Nievergelt J, Santos S, Suter UW. *J Chem Phys* 2001;114:9764.
- [12] Santos S, Suter UW, Müller M, Nievergelt J. *J Chem Phys* 2001;114:9772.
- [13] Khare R, Paulaitis ME, Lusting SR. *Macromolecules* 1993;26:7203.
- [14] Rapold RF, Mattice WL. *J Chem Soc Faraday Trans* 1995;91:2435.
- [15] Clancy TC, Mattice WL. *J Chem Phys* 2000;112:49.
- [16] Pant PVK, Theodorou DN. *Macromolecules* 1995;28:7224.
- [17] Mavrantzas VG, Boone TD, Zervopoulou E, Theodorou DN. *Macromolecules* 1999;32:5072.
- [18] Uhlherr A, Mavrantzas VG, Doxastakis M, Theodorou DN. *Macromolecules* 2001;34:8554.
- [19] Karayiannis NC, Mavrantzas VG, Theodorou DN. *Phys Rev Lett* 2002;88:105503.
- [20] Karayiannis NC, Giannousaki AE, Mavrantzas VG, Theodorou DN. *J Chem Phys* 2002;117:5465.
- [21] Curcó D, Alemán C. *J Chem Phys* 2003;119:2915.
- [22] Curcó D, Alemán C. *J Comput Chem* 2004;25:790.
- [23] Curcó D, Laso M, Alemán C. *J Phys Chem* 2004;108:20339.
- [24] Siepmann JI, Frenkel D. *Mol Phys* 1992;75:59.
- [25] de Pablo JJ, Laso M, Suter UW. *J Chem Phys* 1992;96:2395.
- [26] Laso M, de Pablo JJ, Suter UW. *J Chem Phys* 1992;97:2817.
- [27] Curcó D, Alemán C. *J Chem Phys* 2004;121:9744.
- [28] Curcó D, Alemán C. *J Polym Sci Polym Phys* 2006;44:953.
- [29] Dodd LR, Boone TD, Theodorou DN. *Mol Phys* 1993;78:961.
- [30] Leontidis E, de Pablo JJ, Laso M, Suter UW. *Adv Polym Sci* 1994;116:283.
- [31] Curcó D, Casanovas J, Roca M, Alemán C. *Comput Phys Commun* 2005;169:335.
- [32] Wu MG, Deem MW. *J Chem Phys* 1999;111:6625.
- [33] Manocha D, Zhu Y, Wright W. *Comput Appl Biol Sci (CABIOS)* 1995;11:71.
- [34] Canutescu AA, Dunbrack Jr RL. *Protein Sci* 2003;12:963.
- [35] Coutsias EA, Seok C, Jacobson MP, Dill KA. *J Comput Chem* 2004;25:510.
- [36] Cortés J, Siméon T, Remaud-Siméon M, Tran V. *J Comput Chem* 2004;25:956.
- [37] van den Bedem H, Lotan I, Latombe JC, Deacon AM. *Acta Cryst D* 2005;61:2.
- [38] Shehu A, Clementi C, Kavraki LE. *Proteins* 2006;65:164.
- [39] Porta JM, Ros L, Thomas F, Corcho F, Cantó J, Pérez JJ. *J Comput Chem* 2007;29:144.
- [40] Lee HY, Liang CG. *Mechanism and Machine Theory* 1988;23:209.
- [41] Renaud M. In: Hassan MF, Megahed SM, editors. *Current advances in mechanical design and production VII*. Pergamon; 2000. p. 15–25.
- [42] Renaud M. *Calcul des modèles géométriques inverses des robots manipulateurs 6R*. Rapport LAAS N°06332; 2006.
- [43] Manocha D, Canny JF. *IEEE J Robotics Automat* 1994;10:648.
- [44] Golub GH, Van Loan CF. *Matrix computations*. 3rd ed. Baltimore: Johns Hopkins University Press; 1996.
- [45] Anderson E, Bai Z, Bischof C, Blackford S, Demmel J, Dongarra J, et al. *LAPACK users' guide*. 3rd ed. Philadelphia, PA: Society for Industrial and Applied Mathematics; 1999.
- [46] Weiner SJ, Kollman PA, Nguyen DT, Case DA. *J Comput Chem* 1986;7:230.
- [47] Flory PJ. *In statistical mechanics of chain molecules*. New York: Wiley Interscience; 1969.
- [48] Mattice WL, Suter UW. In *Conformational theory of large molecules. The rotational isomeric State model in macromolecular systems*. New York: John Wiley & Sons Inc.; 1994.
- [49] Curcó D, Alemán C. *J Comput Chem* 2007;28:129.