

# A novel geometric embedding algorithm for efficiently generating dense polymer structures

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A new algorithm for generating starting polymer structures for molecular simulations (e.g., MD) in dense phase is presented. The algorithm yields structures that fulfill to a large extent rotational isomeric state (RIS) probabilities and avoid atomic overlap. The heuristic search bases on the new parallel-rotation (ParRot) technique. We tested the performance of the algorithm on two polymeric systems: Atomistic polyethylene and polystyrene. The algorithm permits to tackle the problem of packing chains into large boxes of size up to 50 Å in a couple of hours on common workstations. Moreover, our packing algorithm is applicable for general polymer systems. The algorithm requires CPU effort scaling with a power 2.8 in the chain length, and with a power 1.5 in the number of chains. © 2001 American Institute of Physics. [DOI: 10.1063/1.1371480]

## I. INTRODUCTION

All bulk properties of polymers are dependent on a number of different factors, prominent among them the chemical structure as well as the arrangement of the macromolecules in a dense packing. In principle, all simulations should be ergodic and it should not matter with which configuration one begins. In practice, however, since it is very difficult to completely change the starting structure during the simulation of dense atomistically detailed polymer systems, one should start with a reasonably “good” structure.

We measure the quality of a polymer structure by comparing its distribution of torsion angles to the probabilities given by the rotational isomeric state (RIS) model.<sup>1,2</sup> The problem consists of creating a packing of polymers that agrees with the RIS probabilities where the chains do not intersect themselves and also do not intersect their periodic images. The task of generating dense polymer systems is formidable due to the high density and the connectivity of the polymer systems.

Much effort has been put into constructing “reasonable” amorphous packings starting from atomistic models of single polymer chains. Common approaches can be roughly divided into four groups. The first comprises methods that grow chains into dense phases by adding new segments according to a choice criterion for achieving the target chain properties.<sup>3,4</sup> A second group starts from coarse “initial guesses” created on a lattice.<sup>5</sup> A third departs from structures with very low densities that are then condensed step by step during  $NpT$ -MD simulation to experimental densities of polymer systems.<sup>6,7</sup> An alternative technique, described recently, starts by preparing the monomer liquid in the periodic box and then polymerizing the monomers to a chain.<sup>8</sup> Common to these methods<sup>9</sup> is that the “initial guess” structures are subsequently relaxed by potential energy minimization or

simulated annealing where the temperature is gradually reduced to that of interest.

Today, the problem mainly lies in the generation of the initial-guess structure. The initial guess does not match experimental statistical data or it loses its imposed statistical properties during “condensation” and relaxation.

In this article, we describe an alternative approach for generating polymer chains that avoids atomic overlaps, and increases the tendency of the chains to obey the proper chain statistics. The idea is to start with a random conformation to be improved iteratively by means of a heuristic search algorithm, which ultimately furnishes the target conformation. We split the packing problem into a sequence of problems with increasing difficulty. A horizon parameter defines the range beyond which the atoms do not perceive each other. It is increased to eventually attain its full range where each atom can “see” all others. Besides this incremental modification of the nonbonded interactions between the atoms, the performance of the search algorithm relies heavily on the efficiency of the moves used during the exploration in the search space of conformations. We devised a new move, the parallel rotation (ParRot),<sup>10</sup> for efficiently relaxing the torsion angles that are deep inside long chains in dense systems. We prove this move to contribute to a large extent to the success of our algorithm.

As an illustration, we apply the method to study polyethylene molecules of varying lengths. This polymer is widely used commercially, and its structure has been studied extensively by a variety of methods. To demonstrate the efficiency of our new method for large system sizes at high density, we generate several realizations for systems of varying size, and analyze the quality of the final conformations.

In addition, we show, for the first time, that dense conformations of atomistic polystyrene chains can be generated

that correspond to a large extent to experimental statistical data and that largely preserve these properties during subsequent molecular dynamics simulations.

## II. A GEOMETRIC MODEL OF POLYMER CHAINS

We approach the polymer packing problem as a geometric optimization problem. The chemical force field is transformed into a set of geometric and statistical constraints. This transformation is an effective filter that simplifies the problem by selecting only relevant properties of the initial system.

### A. Torsion angle space

Any molecular system can be uniquely described by the set of Cartesian coordinates for its atoms. Alternatively one can choose to describe the same system in “internal” coordinates (i.e., bond lengths, bond angles, torsion angles, and a few position and orientation coordinates).

In the case of polymer chains, it has been shown that bond lengths and bond angles are usually confined to a narrow range about a mean value, and they can, therefore, often be considered to be constant for most analyses of flexible chains. Thus, we restrict ourself by considering the torsion angles to be the only degrees of freedom for the system (besides the overall molecular positioning parameters).

The use of the so-called generalized coordinates, popularized by Flory<sup>1</sup> and others, considerably facilitates the description of any molecular structure. We introduce rigid groups for describing the conformations in our simulations. Rigid groups are sets of atoms whose relative positions cannot be modified by changing the torsion angles. A molecular structure can always be split into a set of rigid groups connected by torsion angles. The bond (with variable torsion angle) connecting two rigid groups is termed a free bond. Rigid groups and free bonds build a tree structure where rigid groups are the vertices and free bonds the edges. (see Fig. 1).

A rigid group  $g^{(i)} := \{r_1^{(i)}, \dots, r_{k_i}^{(i)}\}$  in the molecule  $i$  is defined as the set of relative coordinates  $r_j^{(i)}$  for the  $k_i$  atoms comprised in the rigid group. We can entirely describe the molecule  $i$ , composed of a set of rigid groups  $g_k^{(i)}$ , by an origin vector  $r_0^{(i)}$ , three Euler angles  $\alpha^{(i)}$ ,  $\beta^{(i)}$ , and  $\gamma^{(i)}$ , and a vector of  $N$  values for the torsion angles,

$$D^{(i)} := \{r_0^{(i)}, \alpha^{(i)}, \beta^{(i)}, \gamma^{(i)}, \Phi_1^{(i)}, \dots, \Phi_N^{(i)}\}. \quad (1)$$

Then, the conformation of a system of  $M$  molecules is specified by  $D = \{D^{(1)}, \dots, D^{(M)}\}$ .

### B. Rotational isomeric state model

The rotational isomeric state (RIS) model<sup>1,2</sup> makes possible the description of the conformational behavior of macromolecules with proper attention to the details of the chemical structure of the chain. In the RIS model, the possible values for torsion angles are restricted to sets of discrete values. These RIS states, together with values for the correlations of (usually) two adjacent torsion angles along the polymer backbone, allow us to properly account for the chemical details of different polymer structures. Here, the

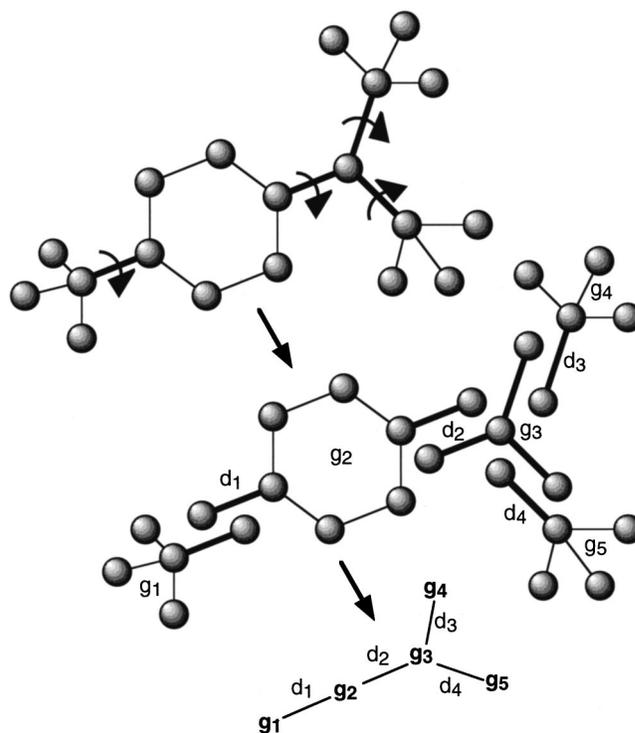


FIG. 1. Tree view of a molecule: Rigid groups of atoms are nodes connected by torsion angles that can be freely rotated.

RIS model is somewhat relaxed insofar as the torsion angles are not required to exactly assume a given RIS state, but are allowed a certain tolerance around that state (say,  $\pm 25^\circ$ ).

### C. Steric exclusion interaction

To generate dense configurations of polymers, one has to account for the nonbonded interaction. We replaced the van der Waals potential function by a hard-sphere potential. This can be done for each atom type by adjusting the potential parameters to accurately approximate the virial equation of state for a gas of suitably selected structure.<sup>11</sup> The hard-sphere potential is a local type of interaction, and, thus, does not require expensive computations. Infinitely extended dense systems of polymer chains are usually modeled by a box that is replicated throughout space to form an infinite lattice of boxes. The periodic system constitutes the target unit cell in which the polymer chains have to be eventually embedded.

### D. The polymer packing problem

The polymer packing problem can now be formulated as an optimization problem. Given a target density, a number of polymer chains, and the corresponding RIS states with their distribution, we devise an algorithm for finding a set of torsion angles for which the following conditions hold:

- (1) The density of the periodic system corresponds to the imposed one;
- (2) The hard-spheres are not overlapping;
- (3) The pairwise distribution for the torsion angles given by the RIS model is respected.

### III. THE SEARCH ALGORITHM

The search algorithm PolyPack we present has been designed to generate starting configurations of dense systems of atomistically detailed molecules.

The input of PolyPack consists of a description of the molecules' structure in terms of rigid groups and rotatable bonds together with the desired pairwise distribution of adjacent torsion angles. The distribution matrices are derived from the statistical weights of the RIS model used. Additionally, the number  $M$  of molecules to be packed and the side length  $L$  of the cubic periodic box need to be specified.

The output of PolyPack is a set of coordinates for all atoms of the system that (i) avoids (as far as possible) severe overlaps of atoms; (ii) matches the given correlations for the preselected RIS states.

#### A. The optimization target

To measure the quality of a system conformation, we introduce a penalty or cost function inspired by the hard-sphere type of interaction. The collision function  $\text{coll}(k, l)$  between two atoms  $k$  and  $l$  measures the fractional overlap of the two hard spheres relative to the sum of the two hard-sphere radii,

$$\text{coll}(k, l) := \max \left\{ 0, 1 - \frac{\|\mathbf{r}_k - \mathbf{r}_l\|_L}{r_k^0 + r_l^0} \right\}, \quad (2)$$

where  $r_k^0$  and  $r_l^0$  are the hard-sphere radii for the atoms  $k$  and  $l$ , respectively, and  $\mathbf{r}_k$  and  $\mathbf{r}_l$  their location. The distance  $\|\mathbf{r}_k - \mathbf{r}_l\|_L$  is measured according to the minimum image convention<sup>12</sup> for a system in a box of side length  $L$ .  $\text{Coll}(k, l)$  is 1 when two atoms' centers share the same locus and 0 if the two atoms do not overlap.

It is hardly possible in practice to find a "reasonable" configuration by starting any search with a random conformation and taking into account all collisions from the beginning. Furthermore a small change of one torsion angle can cause a large number of atoms to move and consequently many collisions to arise.

To overcome this problem, we reduce at first the number of considered collisions and gradually increase that number to eventually include the full range of interactions among the atoms. This can be achieved by limiting the "horizon"  $h$  beyond which pairs of atoms are "ghosts" to each other. If two atoms of the same molecule are considered, they are linked by a series of free bonds. If the number of free bonds along the shortest path joining these two atoms is larger than the horizon value  $h$ , the collision contribution of this atom pair is ignored.

In the case of a pair of atoms belonging to different molecules, the intermolecular collision is considered only if both atoms are structurally separated by less than  $h/2$  free bonds from their molecule's central free bond. That way overlaps between atoms near the center of a molecule can be eliminated in early stages of the search.

The overall penalty or cost function  $\text{cost}(D, h)$  of a conformation  $D$  is defined as the maximum value of the collision function over all possible atom pairs within a given horizon  $h$ . The cost function reads

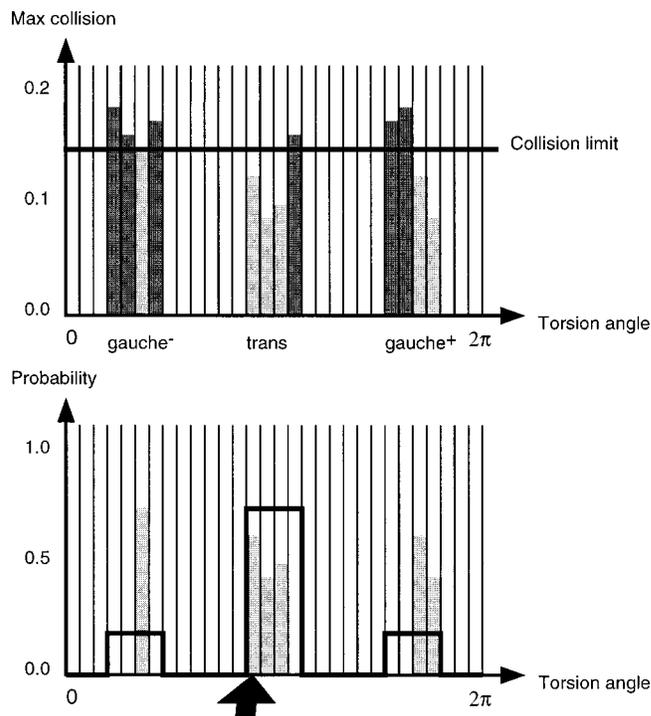


FIG. 2. Sketch illustrating the optimization of a single move: All angles outside RIS intervals or with maximum collision above the collision limit are eliminated. The algorithm selects one of the remaining angles according to their probabilities.

$$\text{cost}(D, h) := \max_{(k, l): \text{atom pair within } h} \text{coll}(k, l). \quad (3)$$

The value of the cost function can be large even though only a single pair of atoms overlaps.

#### B. The optimization strategy

The search algorithm addresses the problem of minimizing the cost function  $\text{cost}(D, h)$  under the constraint of the given RIS probabilities of torsion angle pairs.

If a move is attempted where a particular torsion angle  $\Phi_i$  is modified, the given RIS probability permits us to calculate the relative frequency  $\text{prob}(D, \Phi_i)$  for this new configuration to occur. Due to the correlations between neighboring torsion angles in the RIS model, it depends on the local configuration of torsion angles around the angle  $\Phi_i$ .

The basic optimization step of PolyPack consists of the optimization of all torsion angles in random order. When a torsion angle  $\Phi_i$  is chosen, the algorithm systematically scans the set of its RIS states. For each position of  $\Phi_i$ , the cost function  $\text{cost}(D, h)$  and the probability  $\text{prob}(D, \Phi_i)$  of the new conformation  $D$  is evaluated.

First, all the values of  $\Phi_i$  that cause collisions that exceed a set threshold  $c_{\text{goal}}$  are eliminated. In a second step, the algorithm picks one of the remaining values according to their probabilities  $\text{prob}(D, \Phi_i)$ . If none of the RIS states decreases the collision below the threshold  $c_{\text{goal}}$ , then the one angle giving the lowest collision value is chosen (see Fig. 2). The parameter  $c_{\text{goal}}$  is analogous to a temperature parameter in a physical system. It permits us to overcome cost-function barriers.

### C. The search loops

The search starts with an arbitrary structure. In the innermost loop, the steric aspects of the packing are iteratively improved by performing optimization steps based on different types of moves. The iteration continues until the collision function  $\text{coll}(D, h)$  attains a local minimum or reaches a lower limit. Explicitly we have

```

procedure Optimize ( $D, c_{\text{goal}}, h$ );
begin
  repeat
    forall move  $\in$  set of moves do
      Optimization Step ( $D, \text{move}, c_{\text{goal}}, h$ );
    endfor
  until ( $\text{cost}(D, h) \leq c_{\text{goal}}$ ) or configuration  $D$  not
    changed;
end.

```

If none of the attempted optimization steps can decrease  $\text{cost}(D, h)$  below  $c_{\text{goal}}$ , it means that the search path is trapped in a (almost certainly local) minimum. To overcome the barriers of the cost function in the high-dimensional configuration space, we opted for a local disturbance of the system similar to a sudden increase in temperature, which would randomize the system. The Disturb procedure consists of an instantaneous increase of the collision limit  $c_{\text{goal}}$  followed by a step-by-step reduction of  $c_{\text{goal}}$  until its original value is reached again. It turns out to be a robust method to escape local minima:

```

procedure Disturb ( $D, c_{\text{goal}}, h$ );
begin
   $D_{\text{save}} \leftarrow D$ ;
   $c_{\text{disturb}} \leftarrow (\text{cost}(D, h) + c_{\text{offset}})$ ;
  repeat
    Optimize ( $D, c_{\text{disturb}}, h$ );
    if  $\text{cost}(D, h) \leq c_{\text{disturb}}$  then  $c_{\text{disturb}} \leftarrow (c_{\text{disturb}} - c_{\text{delta}})$ ;
  until  $c_{\text{disturb}} \leq c_{\text{goal}}$  or configuration  $D$  not changed;
  if  $\text{cost}(D_{\text{save}}, h) < \text{cost}(D, h)$  then  $D \leftarrow D_{\text{save}}$ ;
end.

```

In the case where Disturb fails to improve the structure, the procedure automatically returns the original structure. We now have all ingredients to formulate the complete embedding algorithm:

```

procedure HorizonLoop( $D, c_{\text{goal}}$ );
begin
  Construct an appropriate starting structure  $D$ ;
  for  $h \leftarrow 0$  to  $h_{\text{max}}$  by step  $h_{\text{step}}$  do
    trial  $\leftarrow 1$ ;
    repeat
      Optimize ( $D, c_{\text{goal}}, h$ );
      if  $\text{cost}(D, h) > c_{\text{goal}}$  then
        Disturb ( $D, c_{\text{goal}}, h$ );
      endif
      trial  $\leftarrow$  (trial + 1);
    until trial  $>$  trialmax or  $\text{cost}(D, h) < c_{\text{goal}}$ ;
  endfor
end.

```

The starting structure is constructed by choosing torsion angle values according to the RIS probabilities. This proce-

dure easily applies to ghost chains. For each value of  $h$  from 0 to  $h_{\text{max}}$ , an optimization step is performed. If one of those optimization steps does not succeed, the Disturb procedure is used. Since the efficiency of the algorithm strongly relies on the capabilities of the moves performed at each optimization stage to relax the torsion angles, a careful choice of those moves is necessary.

### D. Optimization moves

Five moves have been used in our algorithm (see Fig. 3). The simplest one in the framework of generalized coordinates is a single rotation that modifies one torsion angle at a time.

Despite its simplicity, this move suffers major drawbacks. The displacement of atoms far from the rotating angles can be tremendous especially when the torsion angle lies inside a long chain and the rotating part of the molecule changes its orientation with regard to the periodic box. This change of orientation can cause severe atom overlaps due to the periodicity.

As an alternative, we devised the Parallel Rotation (ParRot) move.<sup>10</sup> ParRot modifies torsion angles in long chains without creating severe atom overlaps. This can be achieved if all the atoms of the moving segment of a chain are displaced by the same vector. Four subsequent torsion angles are modified simultaneously such that the orientation of the moved segment remains the same as that in its original position.

The two next moves treat a single rigid object. The entire molecule can be translated by a small displacement vector, or rotated around its center of mass (see Fig. 3). The first move modifies the global position of the chain, the second one its orientation. No torsion angles are changed.

The last move has been introduced to account for specific molecular structures. Certain polymer chains consist of rings along their backbone. The rigid group comprising the ring is connected to its neighboring rigid groups by two collinear bonds. In this case, when the two torsion angles

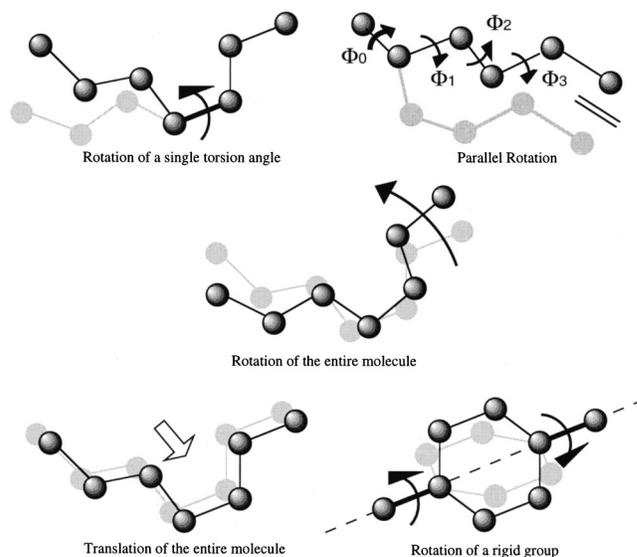


FIG. 3. Moves used by the packing algorithm.

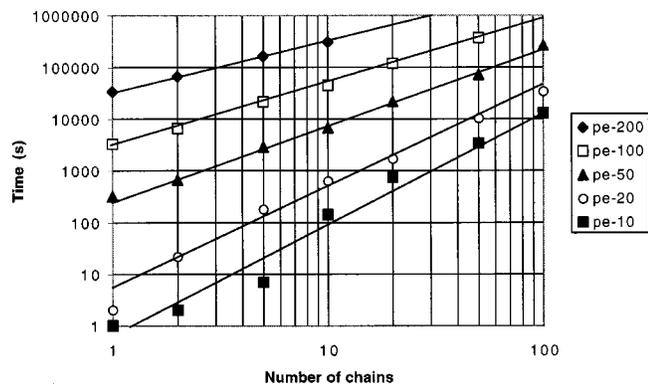


FIG. 4. Relative computing time in function of the number of chains of the system. "pe- $n$ " refers to polyethylene chains of  $n$  methylene units.

around the ring are varied by the same amount but in opposite directions, the ring merely rotates isolated from the rest of the molecule. This group rotation move is of high efficacy for particular molecular structures.

### E. Implementation

PolyPack is available as a software package. The first stage of any molecular simulation consists in creating a template for the molecular structure to be simulated. We assume this structure template to comply to the MSI/Biosym file formats of "mdf" and "car" files. A conversion tool parses these files and generates the description file needed by PolyPack. It contains the rigid group decomposition of the molecule, the atoms' hard sphere radii, and the RIS states for each torsion angle together with the probabilities and pairwise correlations matrices. PolyPack reads the description file and generates coordinates in the standard "car" format which serves as input of subsequent standard (e.g., molecular-dynamics) simulations.

## IV. RESULTS AND DISCUSSION

We tested the scaling behavior of the computing time, the effects of the packing methods and the accuracy of the results of PolyPack by applying it to systems of polyethylene molecules of various sizes at density  $0.892 \text{ g/cm}^3$ .

As a second test case we discuss isotactic polystyrene, a rather complex polymer. All known simulated three-

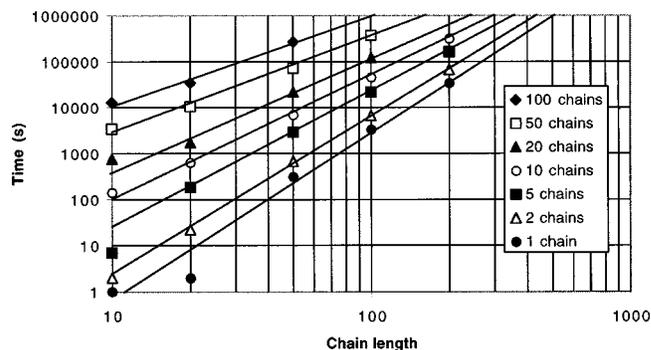


FIG. 5. Relative computing time in function of chain lengths.

dimensional conformations of polystyrene deviate from the experimentally ascertained solid-state torsion angle distributions. It therefore constitutes a great challenge for PolyPack.

### A. Measured time complexity

Figure 4 displays the growth of computing time of PolyPack with the number of chains. The computational effort in function of the length of the chains is shown in Fig. 5.

From the bilogarithmic plots, the relative computing time  $t$  appears to be polynomial, both in the number of molecules  $M$  and the length of the molecules  $N$ ,

$$t \propto M^\mu \cdot N^\nu, \quad (4)$$

with  $\mu = 1.5 \pm 0.2$  and  $\nu = 2.8 \pm 0.2$ . Attention should be paid to the fact that the complexity of the packing algorithm is polynomial although the search space, that is, the number of possible conformations, grows exponentially with the number of degrees of freedom. As an example for the absolute CPU effort, a system of 50 polyethylene chains of 100 repeat units with a box size of  $50 \text{ \AA}$  could be successfully packed in 3 days on an SGI-R5000 workstation.

### B. Effects of packing techniques

In previous sections, we described a variety of methods to improve the packing of macromolecules. Since most of these methods have a heuristic character, it is difficult to predict their effect on the convergence of the algorithm. We measured the effects of the important ingredients of the al-

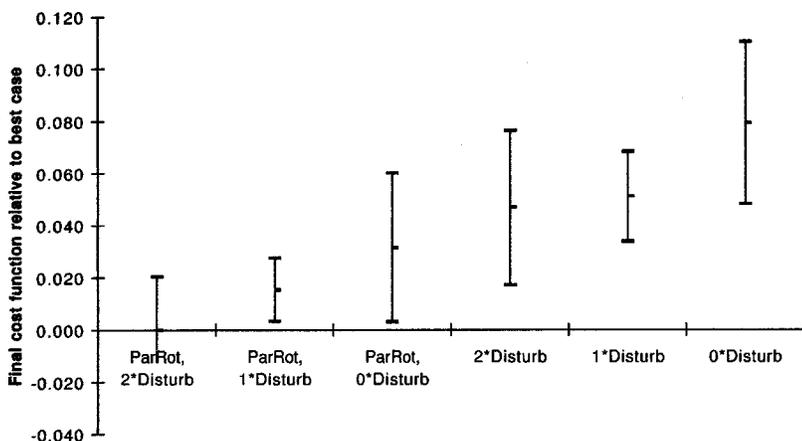


FIG. 6. Effects of Disturb and ParRot on the maximum collision value of the generated packings.

gorithm (ParRot, Disturb, and the horizon parameter) and compared their performances on a given system of 10 polyethylene chains of 50 repeat units each. The system contains 1520 atoms and 500 torsion angles.

To measure the effectiveness of ParRot and Disturb, we started PolyPack with and without using the ParRot move and with zero, one, or two calls to Disturb at each horizon value. For all six variants, we packed the system of polyethylene chains 20 times, each time with a different starting conformation. Each run produced a packing with a final maximum overlap value. The average overlaps as well as the standard deviations over the 20 runs are shown in Fig. 6. The omission of the ParRot move as well as the Disturb method each increases the final overlap by about one standard deviation, indicating that both techniques improve the performance of PolyPack significantly.

In Sec. III C the parameter  $h_{\text{step}}$  was introduced. It defines the amount by which the horizon parameter  $h$  is increased during the outermost loop of the packing algorithm. Since the chains of our test system consist of 50 repeat units and 50 torsion angles on the backbone, the maximum value for the horizon parameter  $h_{\text{max}}$  is 50. If  $h_{\text{step}}$  is set to 1, the system is optimized for all horizon values from 0 up to 50. This strategy is very time consuming, but it produces the most accurate results. On the other hand, if  $h_{\text{step}}$  is 50, the concept of a horizon parameter is eliminated since the system is optimized only once, considering all atom collisions from the beginning.  $h_{\text{step}}$  is used to control the trade off between the computing time and the quality of the generated structure. Figure 7 presents the average over collision values of 10 runs, as well as their standard deviation for several step sizes ranging from 1 to 50.

### C. Effects of moves

As mentioned in Sec. III D, our algorithm makes use of five different moves. We measured the effectiveness of a particular move as the ratio of the number of times it succeeded in improving the system (reducing the maximum collision) relative to the total number of times it was employed during the packing process. Figure 8 shows this success ratio for all moves described vs the value of the horizon param-

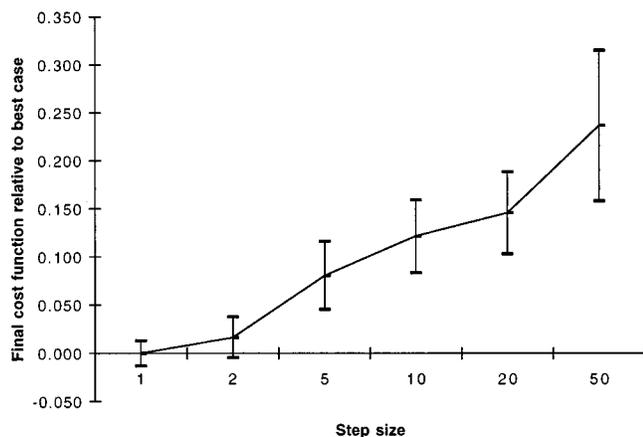


FIG. 7. Effect of the variation of the horizon step size  $h_{\text{step}}$  on the maximum collision values of the generated packings.

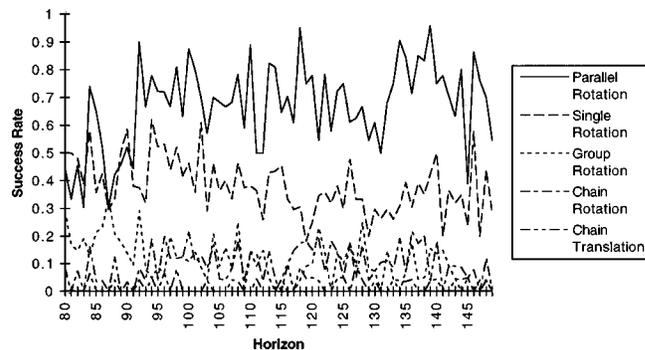


FIG. 8. Success rate of moves with respect to the horizon value.

eter. As expected,<sup>10</sup> the ParRot move outperforms the other moves, especially at the late stages of the packing process when most of the collisions are considered.

### D. Accuracy of results

According to the standard RIS model of polyethylene<sup>1</sup> torsion angles on the backbone are limited to the three RIS states *trans*, *gauche*<sup>+</sup>, and *gauche*<sup>-</sup>. Thus, a pair of two adjacent angles can occupy nine states. The RIS *a priori* probabilities for these states to occur are shown in Fig. 9 as white bars.

We generated 20 different conformations of a system of 10 polyethylene chains composed of 50 methylene units each. The mean value over the maximum overlaps of these 20 structures was 0.216, which means a maximal encountered atom overlap of 21.6% of their hard core radii on average. The average distribution over all pairs of torsion angles of all computed structures is shown in Fig. 9 as data points with standard deviations. The figure shows that PolyPack is able to reproduce a given distribution accurately, even at high densities.

### E. Polystyrene

We used PolyPack to generate conformations of isotactic polystyrene that correspond to given torsion angle distributions. We selected a system composed of 9 chains of 40 monomers each at a density of 1.05 g/cm<sup>3</sup> which corresponds

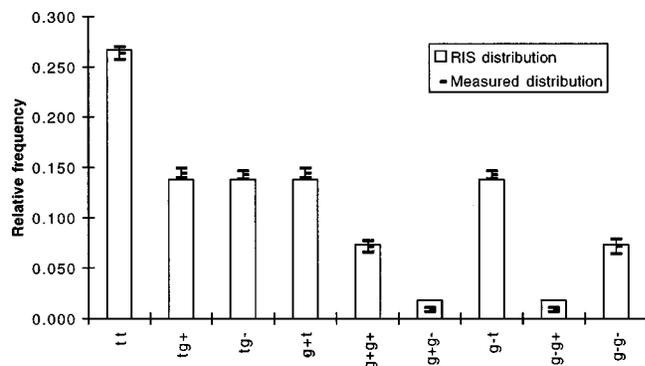


FIG. 9. Agreement of angle distributions with given RIS probabilities for 10 different packings of polyethylene 50.

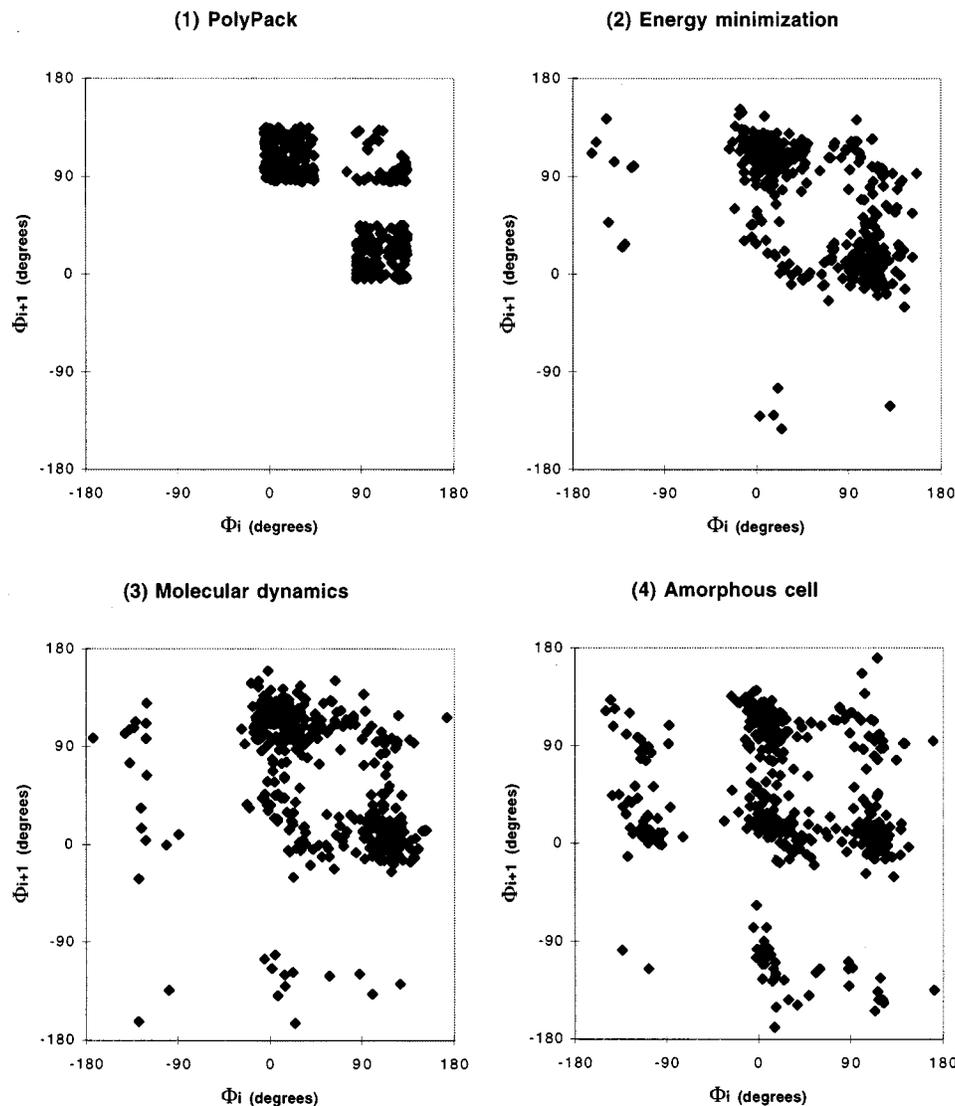


FIG. 10. Distribution of adjacent torsion angles (meso dyads) in glassy amorphous polystyrene.

to a box size of 39 Å. The system comprises 1080 torsion angles and 5778 atoms. The packing process took 18 h on an Ultra-Sparc-II node at 248 MHz.

$P_m$  and  $P_p$  specify the pairwise distribution of the *trans* ( $t$ ) and *gauche* ( $g^+$ ) states of torsion angle pairs attached to the same and to neighboring side chains, respectively. The matrices are derived from Rapold and Suter's 2-state RIS model of polystyrene<sup>2</sup> at 300 K,

$$P_m = \begin{bmatrix} 0.05 & 0.41 \\ 0.41 & 0.13 \end{bmatrix}, \quad (5)$$

$$P_p = \begin{bmatrix} 0.05 & 0.41 \\ 0.41 & 0.13 \end{bmatrix}. \quad (6)$$

The moves used by PolyPack are more restricted than those in typical force fields. Bond lengths and bond angles are kept fixed and torsion angles are restrained to certain intervals. Thus, PolyPack is not able to remove all non-bonded overlaps completely. In subsequent energy minimization and molecular dynamics runs, these overlaps are balanced at the expense of local bond length, bond angle, and torsion angle motions.

Diagram (1) of Fig. 10 gives the distribution of torsion angles of the meso dyads generated by PolyPack with  $\Delta\Phi = \pm 25^\circ$ . It corresponds perfectly to the distribution derived from the RIS model. The relaxation of the strict conformation is illustrated in diagram (2) and (3). They show the distribution of torsion angles after energy minimization and after 20 ps of molecular dynamics simulation at 300 K. The force field employed was PCFF93 by MSI Inc., a force field that reproduces the conformational preferences of the individual chains addressed here well and that gives RIS statistics in agreement with those mentioned above.<sup>2,13</sup> Diagram (4) exhibits the torsion angles of a conformation generated with the commonly used amorphous cell method.<sup>14</sup> In contrast to the distribution in diagram (3), there are significantly more points near the center, which corresponds to the *trans-trans* state, typical for conformations computed with conventional packing methods.

We succeeded in generating conformations of isotactic polystyrene that correspond well to the RIS model (less than 10% *trans-trans* states). They largely maintain this property during subsequent molecular dynamics runs.

## V. CONCLUSION

We described and analyzed a new packing algorithm to generate realistic starting structures of dense polymer systems for Molecular Dynamics and Monte Carlo simulations. The algorithm handles arbitrary, atomistically detailed molecules in the space of generalized coordinates.

We demonstrated that the presented algorithm is able to generate dense packings of polyethylene that do not show large atomic overlaps and agree with given torsion angle statistics. The test systems range from 1 chain of 10 repeat units to 100 chains of 200 repeat units. The CPU effort on a “normal” workstation typically spans a couple of hours to a couple of days.

The CPU effort of the packing algorithm is polynomial in both, the number of molecules to embed and the length of the molecules. We have demonstrated that the packing time for the polyethylene system scales with a power of 2.8 in the chain length and with a power of 1.5 in the number of chains.

The algorithm performs an iterative search in the space of conformations of polymers. The heuristic search procedure makes use of various techniques, such as a horizon parameter for weakening the hard sphere potential, and a “disturbing” technique to avoid the search to remain attracted to local minima in search space. Furthermore, we showed how the newly proposed ParRot move<sup>10</sup> significantly contributes to the success of the packing algorithm.

The new approach to packing consists in considering a local energy model for bonded interactions, formulated in the RIS paradigm. Generated polymer structures result from an optimal balance between obeying RIS correlations for adjacent RIS states and avoiding repelling interactions between nonbonded atom pairs.

Results obtained with isotactic polystyrene indicate the general applicability of the method that goes beyond the simple molecular structure of polyethylene.

## ACKNOWLEDGMENT

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