Two-dimensional random coil chains on hexagonal lattices

V. Mom

Gorlaeus Laboratories, State University, 2300 RA Leiden, PO Box 9502, The Netherlands
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In this article a method of formulating random coil chains that can be used as models of amorphous polymers is described. The method is based on an algorithm that finds self avoiding random (SAR) chains on finite lattices. The lattice constant is chosen to be wide enough to avoid the substituents of the polymer interfering with one another. As an example, the construction of the two dimensional random coil packing structure of polyethylene is discussed. In a following paper three-dimensional models will be treated. The mean squared end-to-end distance of chains, generated with this new method, is linear in the number of lattice points.

INTRODUCTION

In a previous paper[1] a method of constructing SAR chains on finite lattices was described. This method, henceforth called the travelling salesman (TS) method, has a number of advantages over random walk (RW) methods. The TS method is guaranteed to find a chain covering all lattice points using very limited computer time. RW methods have this potential only for small lattices, lattices in which some points have a large number of neighbours or lattices in which almost every point has a coordination number (N_c) of 2.

However, in an intermediate case, for instance a lattice of 300 points with an N_c of 4, a RW method is very time consuming while a fully chained lattice (that is, a lattice of which every point is on the chain) will not be obtained. With the TS method a lattice of 300 points is fully chained in a few seconds CPU time of an Amdahl V7B, the computer that was used for the calculations.

Also, the TS method simulates the physical process of a polymerization much more satisfactorily than RW methods possibly can, because a number of different chains are constructed concurrently. The final number of chains to be constructed is an input parameter and reflects the degree of polymerization desired. If this number is one, then the result of applying the TS method on a lattice is one chain that covers all lattice points once and only once.

To construct a model of polyethylene the tetrahedral lattice, TL, is a good choice. The N_c of every lattice point is 4 and the chain will have bond angles of 109° and dihedral angles of 60°, −60° and 180°, similar to the carbon backbone of polyethylene. However, filling the tetrahedral lattice using the TS method does not result in a good model for polyethylene: if all lattice points are occupied there is no more room available for hydrogen side groups.

Before discussing the actual solution of this problem (see following section) an outline is given of another method that was tested first. This method, resembling the slithering snake method (see ref. 2), runs as follows:

A TL, consisting of N points, is assumed to be fully chained. From the chain an arbitrary part of $N/3$ connected points is chosen to be the carbon backbone and the remaining $2N/3$ points are treated as possible hydrogen positions. For this particular combination of backbone and possible hydrogens a figure of merit is calculated, reflecting as to how far the following criteria are met:

(1) Every carbon point, except for the head and the tail, must have two carbons and two hydrogens as its nearest neighbours.
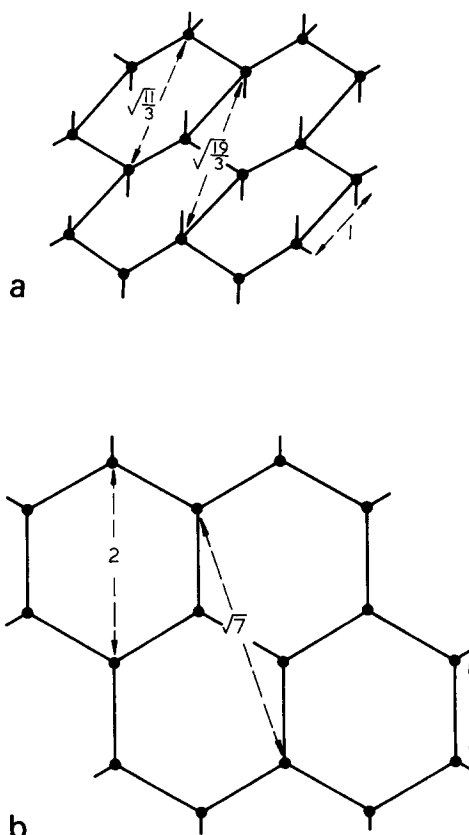
a

b

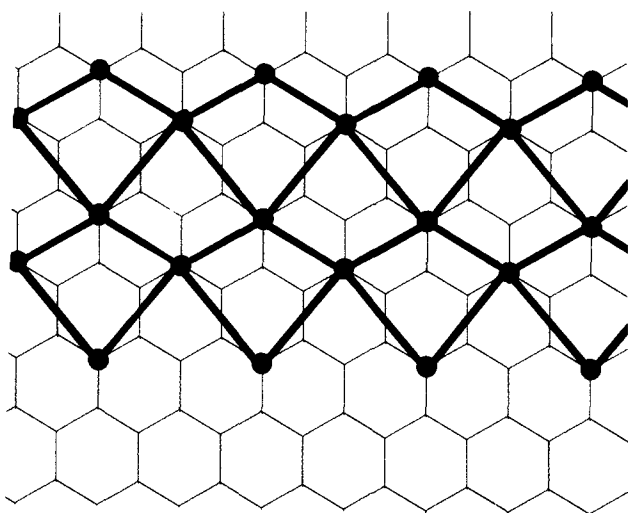*Figure 1* (a) Layer of tetrahedra; (b) projection of layer
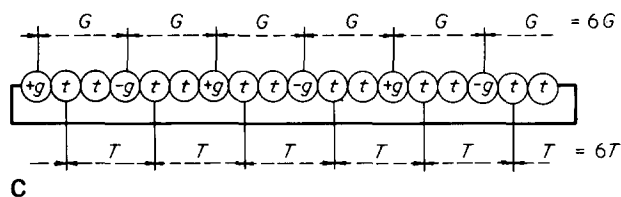
Figure 2 Four edged SL polygon
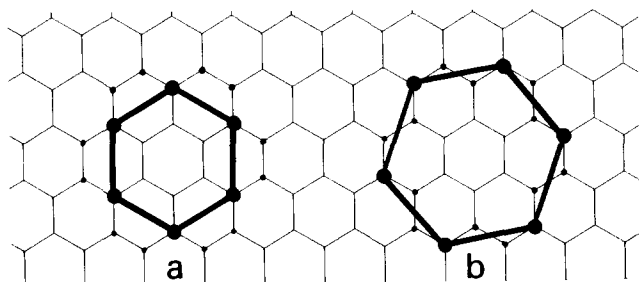
Figure 3 (a) 6*G* polygon; (b) 6*T* polygon; (c) relation between 6*G* and 6*T* polygons

DOUBLE LATTICE METHOD FOR POLYETHYLENE

The philosophy behind the double lattice method is simple. Let TL be the tetrahedral lattice of which every point on completion of the procedure represents a C atom, H atom or a vacancy. From the set TL a subset SL is chosen. This is done in such a manner that a SAR chain in SL constitutes a polyethylene chain in TL. In other words, every segment of the SL chain consists of a number of CH2–CH2 segments. This number, p, and the geometry of SL determine the density of the model.

In this section the principles of the method are explained. For the sake of simplicity this is done using a two-dimensional model. In a subsequent paper the three-dimensional case will be investigated.

For the two-dimensional model two assumptions are made:

(1) Instead of the regular three-dimensional tetrahedral lattice, TL is now an infinite layer of tetrahedra as shown in *Figure 1a*. In the following, TL will be represented by a projection of this layer (*Figure 1b*). Bond lengths in this representation have a value 1.

(2) Every point of SL is a carbon atom in TL.

Now we will determine the value of p and try to find what TL points SL consists of.

The first clue is, that the points of SL form polygons that have edges that are at least 2 units long, corresponding with a *gauche* distance in TL (see *Figure 1b*). In that case $p = 3$. When the length of an edge in SL is less than 2, the hydrogen points connected to the carbon points of this short edge interfere with one another. However, making p larger will decrease both the
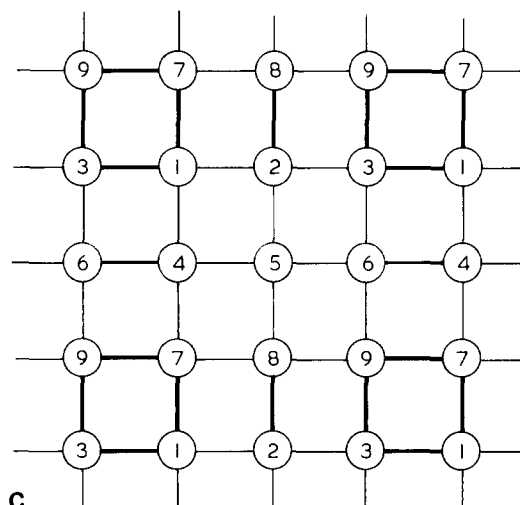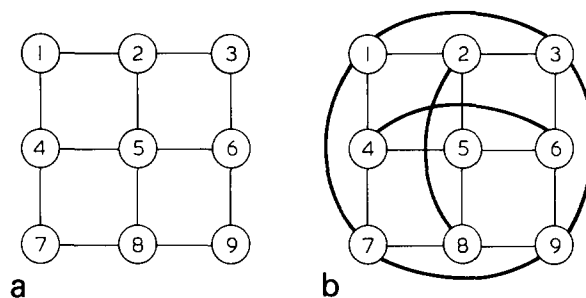
(2) Every hydrogen point must have one and only one carbon as its nearest neighbour.

The second step is to calculate the figures of merit of all possible backbones obtainable by moving the backbone one step along an arbitrary lattice vector. Of this set of new backbones the backbone giving the best result is chosen as the new starting position and the process is repeated until every point of the lattice fulfils either condition 1 or condition 2.

For a lattice of 60 points this method was tried but it failed. Only when the length of the carbon backbone was diminished (this is the same as introducing vacancies) the process produced, within a reasonable amount of time, a partition of carbon atoms, hydrogen atoms and vacancies that was a good representation of a polyethylene molecule. However, the density of the packings generated in this way was too low to be physically realistic (less than 500 kg/m^2). As this method did not give any hope for future progress it was not pursued any further and another method was developed: the double lattice (DL) method.

Figure 4 (a) Lattice; (b) with cyclic boundary conditions; (c) the lattice as a repeating unit
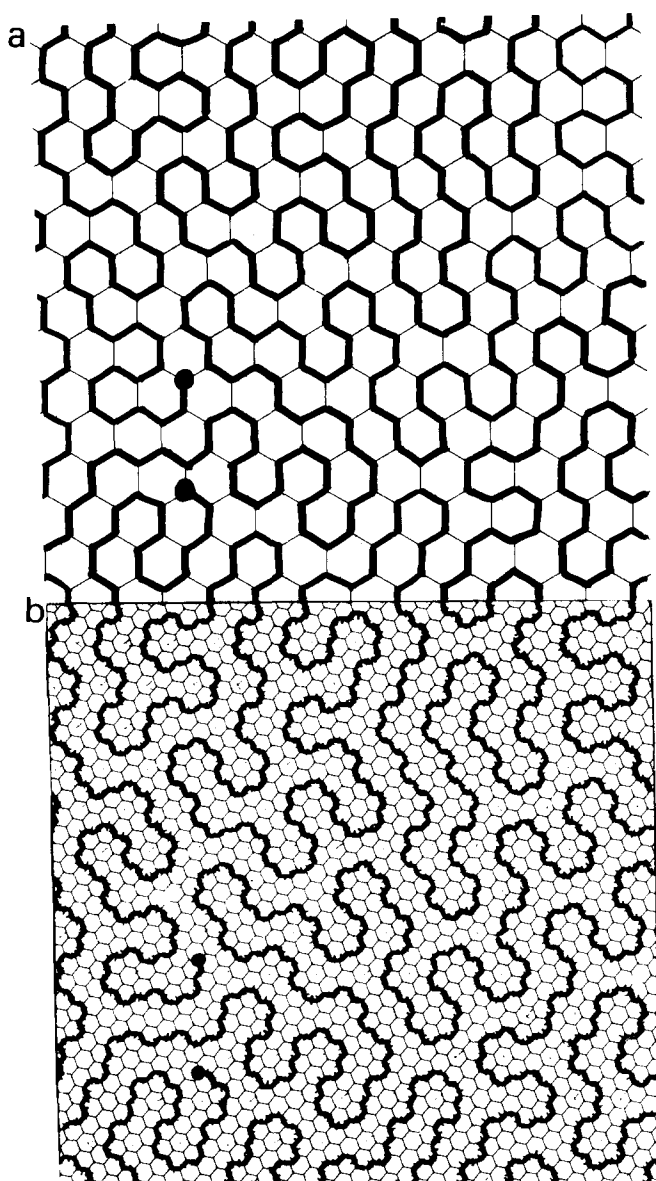
Figure 5 (a) SAR chain on TL lattice; (b) polyethylene carbon backbone on TL1 lattice

randomness and the density of the models, reason enough to keep the value of p as low as possible, preferably 3. In that case the edges of the polygons in SL are either 2 (*gauche* distance) or $\sqrt{7}$ (*trans* distance, see *Figure 1b*).

A solution to the problem may be found as follows: first, polygons having an uneven number of edges, each edge either 2 or $\sqrt{7}$ units long, do not fit in the TL lattice. Secondly, polygons with four edges do not leave room enough for hydrogen. In *Figure 2* one possibility is shown. The SAR chain, covering every point of the SL, accounts for approximately 3/4 of the TL points. This leaves 1/4 for hydrogen points and vacancies, not enough for a polyethylene model.
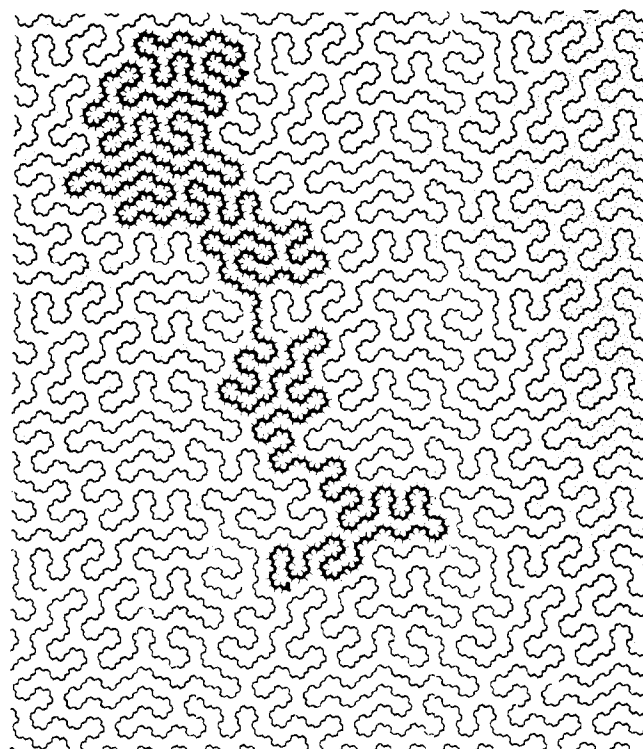

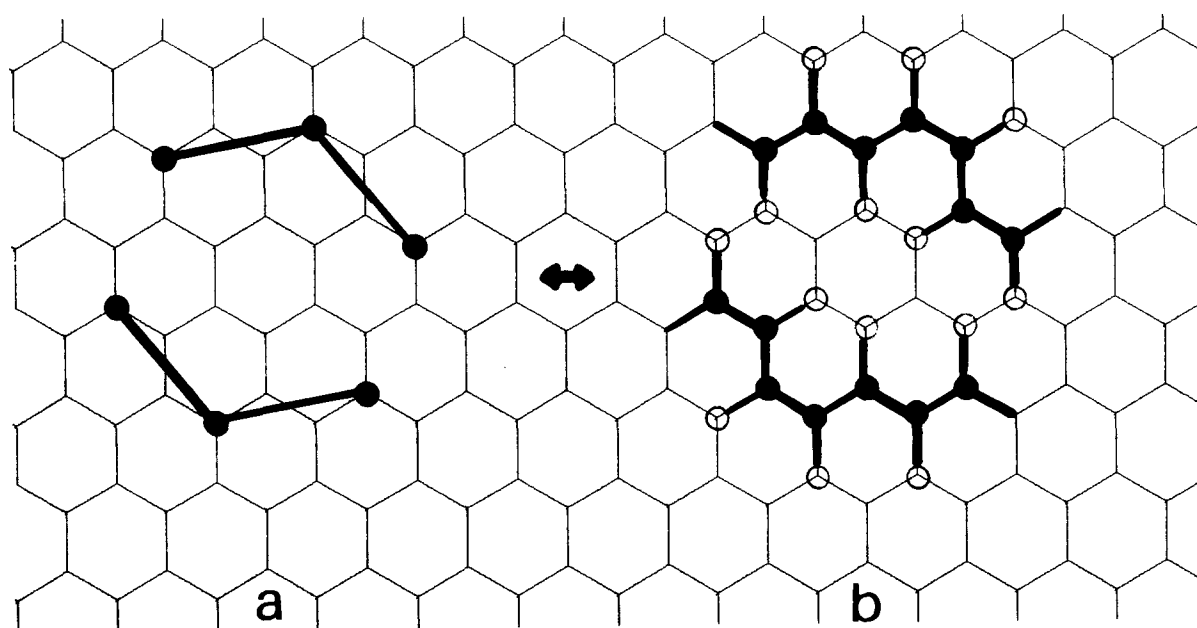*Figure 6* Stretched-out polyethylene model

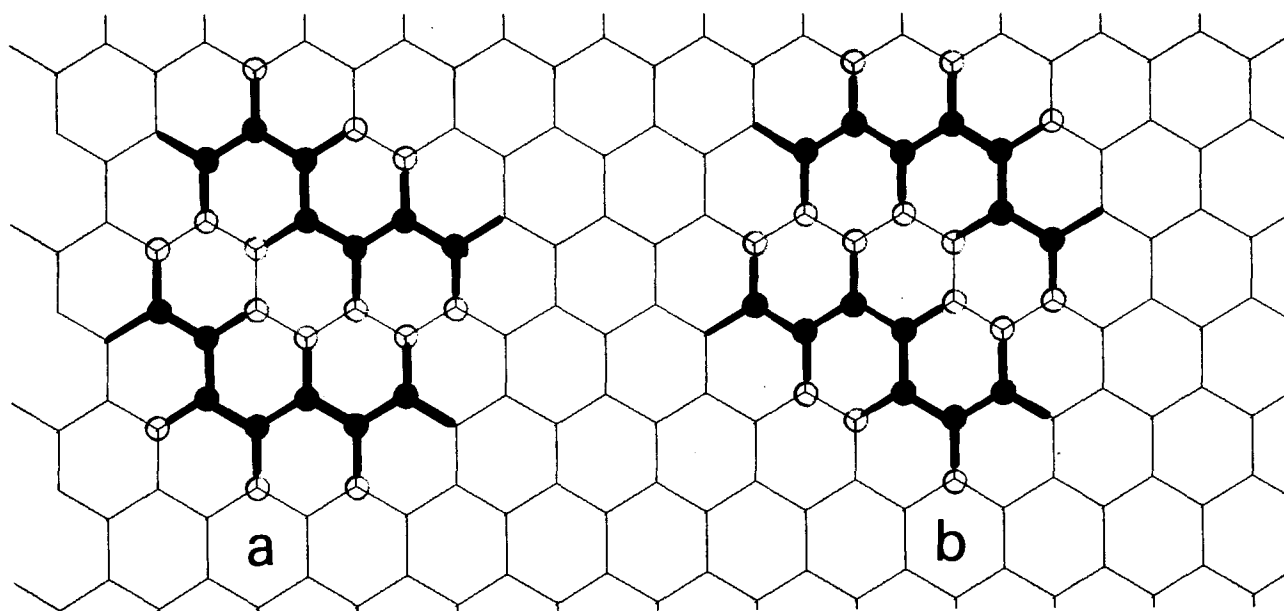*Figure 7* (a) SL conformation; (b) regular TL conformation
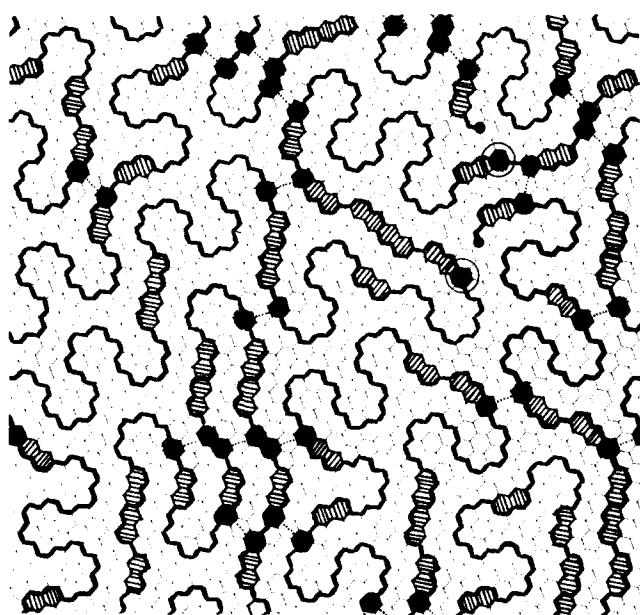
Figure 8 Alternatives for *Figure 7b*

Figure 9 ●- - ▲: pair of sun-glasses and ◉ : monocle (either *Figures 7b, 8a* or *8b*) and ◖◗: either *Figures 10b* or *10c*

To describe the polygons, the following notation will be used: the capitals G and T stand for the *gauche* and *trans* distance respectively, while $+g$, $-g$ and t define what turn a chain takes. So in terms of distances, two sixsided polygons can be constructed in the plane (*Figure 3*). As can be seen, both the *GGGGGG* (6 G for short, *Figure 3a*) and the *TTTTTT* (6T) ring, *Figure 3b*, use the same points of TL. The difference is, that the points of TL that are carbon points lie outside and on the 6G ring, while in the case of the 6T ring an equal number of carbon points is situated inside, outside and on the ring. 6G rings have two thirds of their carbon points outside the ring and, consequently, in that of their neighbours. This gives rise to difficulties filling the plane and 6G rings cannot be used. *Figure 3c* shows how the rings are related to one another.

To keep the polygons in the plane, there must be an even number of *trans* bonds in a sequence between *gauche* bonds that have the opposite sign and an uneven number of *trans* bonds between *gauche* bonds that have the same sign. The sequences $+g-g$ and $-g+g$ are forbidden because the distance between nonbonded carbon points is too small. The sequences $+g+g$, $-g-g$, $+gt+g$ and $-gt-g$ move the polygons out of the plane and therefore they cannot be used. Therefore, the best usable subset SL of TL, with the minimum value of p, is the one built of 6T polygons.

The density of two-dimensional models is a quantity that is not very well defined. However, we can construct an (anisotropic) three-dimensional model by stacking the layers of tetrahedra in which the two-dimensional models reside. If the spacing between two layers is wide enough, taking into accout that every lattice point is occupied by one atom only, it can be shown that the density of such a model is approximately 880 kg/m^3.

AN EXAMPLE

For SL we take a lattice of 364 points (14 by 26) consisting of 6T polygons. Cyclic boundary conditions are used (see *Figure 4*). These cyclic boundary conditions are important to avoid non-equivalence of lattice points[1]. In *Figure 5a* the SAR chain in SL is drawn and in *Figure 5b* the corresponding polyethylene molecule in TL is given. The black chain is the carbon backbone and all the points only one bond distance away from the backbone are the hydrogens. As may be seen, no hydrogen points exist which are connected to more than one carbon point.

Because of the cyclic boundary conditions, *Figure 5a* and *Figure 5b* fit together. This can be done on every side of the picture. The 364 points of the lattice form a repeating unit and by fitting a number of these units together a clear picture of the structure of the polyethylene model (*Figure 6*) is obtained.

A drawback of this model is the regularity, introduced by the 6T rings. However, there is a method to introduce additional irregularity after the generation of the SAR
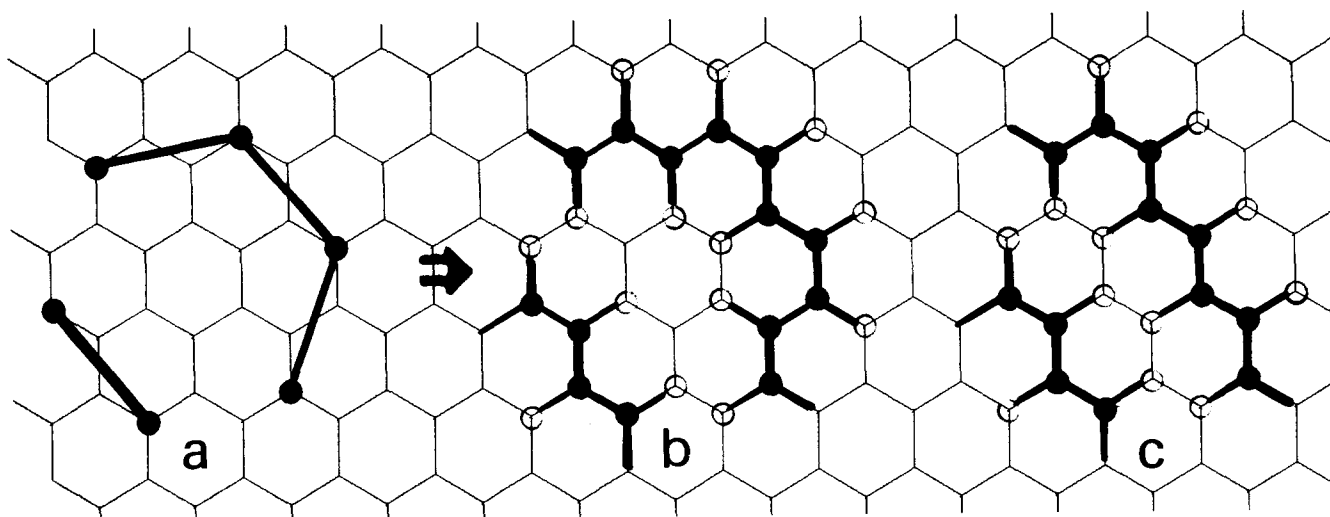
Figure 10 (a) SL conformation; (b) regular TL conformation; (c) alternative to *Figure 10b*

chain. In *Figure 7a* a 6*T* ring in SL is shown of which 4 edges are part of the chain and two are not. In *Figure 7b* the actual conformation in TL is drawn. But in this particular case it is not necessary to use the conformation of *Figure 7b*. There are two other conformations that also fit in the lattice (*Figure 8a* and *8b*). So, after we have constructed the SAR chain in SL, the 6*T* rings that are built like the one in *Figure 7a* are selected and one of the three possible conformations in *Figures 7b, 8a* or *8b* is chosen. In *Figure 9* the places where we can make such choices are shown. For every pair of sun-glasses a choice from the three possible conformations is demanded. Note the two monocles near the end and the beginning of the chain.

In *Figure 10a* another 6*T* ring in SL is shown for which two different conformations in TL exist, *Figure 10b* and *10c*. The conformation in *Figure 10c*, however, has two CH2 groups less than the conformation in *Figure 10b*, so using the *Figure 10c* conformation instead of the regular one lowers the density of the model. In *Figure 9* every pair of crosshatched hexagons stands for either the conformation in *Figure 10b* or the conformation in *Figure 10c*. To display the effect, the polyethylene molecule of *Figure 6* is treated by introducing as much variety as possible, using the conformations in *Figures 8a, 8b* and *10c* instead of those in *Figures 7b* and *10b*. The result is drawn in *Figure 11*.

Another possibility of lowering the density of the model and, at the same time, making room for bulky substituents, is to allow the polygons in SL to have edges longer than 2 or $\sqrt{7}$. SL can, for instance, consist of $TT(\overline{Tt})TT(\overline{Tt})$ rings (*Figure 12a*), $T(\overline{Tt})T(\overline{Tt})(\overline{Tt})(\overline{Tt})$ rings (*Figure 12b*), $TT(T+gt-gt)TT(T+gt-gt)$ rings (*Figure 12c*) or any combination of polygons tiling the plane.

For the hypothetic polymer drawn in *Figure 13* the ring of *Figure 12b* was used to fill SL.

THE MEAN SQUARED END-TO-END DISTANCE AND THE RADIUS OF GYRATION

Physical quantities of polymers such as the mean squared end-to-end distance $\langle R^2 \rangle$ and the radius of gyration D^2 are experimentally accessible. It is therefore interesting to
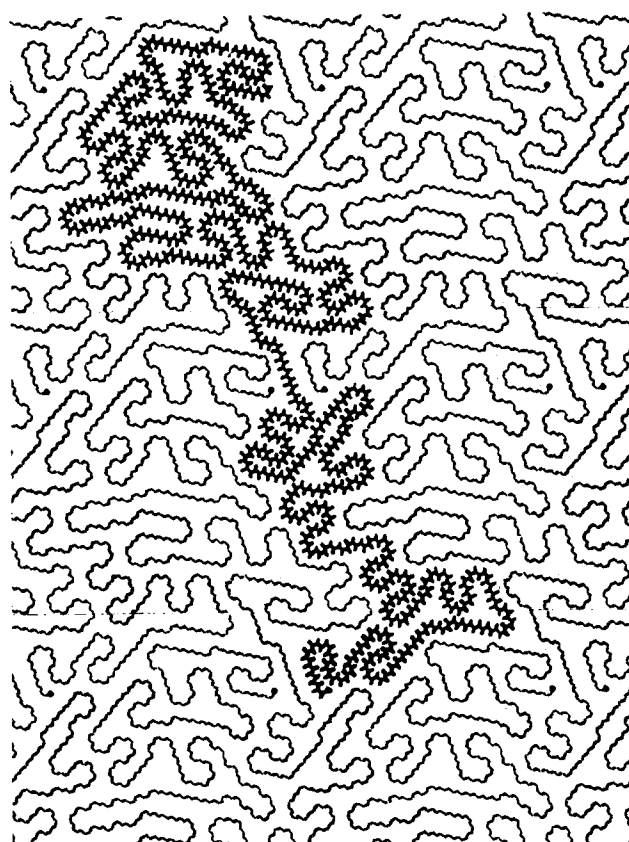

Figure 11 Polyethylene model, with maximum number of alternative conformations

see what rules the corresponding quantities of the models follow.

The mean squared end-to-end distance of unconstrained random walks can be described by[3]

$$\langle R^2 \rangle = c1 * N^{c2} \tag{1}$$

in which $c1$ and $c2$ are constants and N is the number of lattice points. To see whether this expression also is valid for chains that are generated by the TS method a number of chains of different lengths was generated. Seven lattices
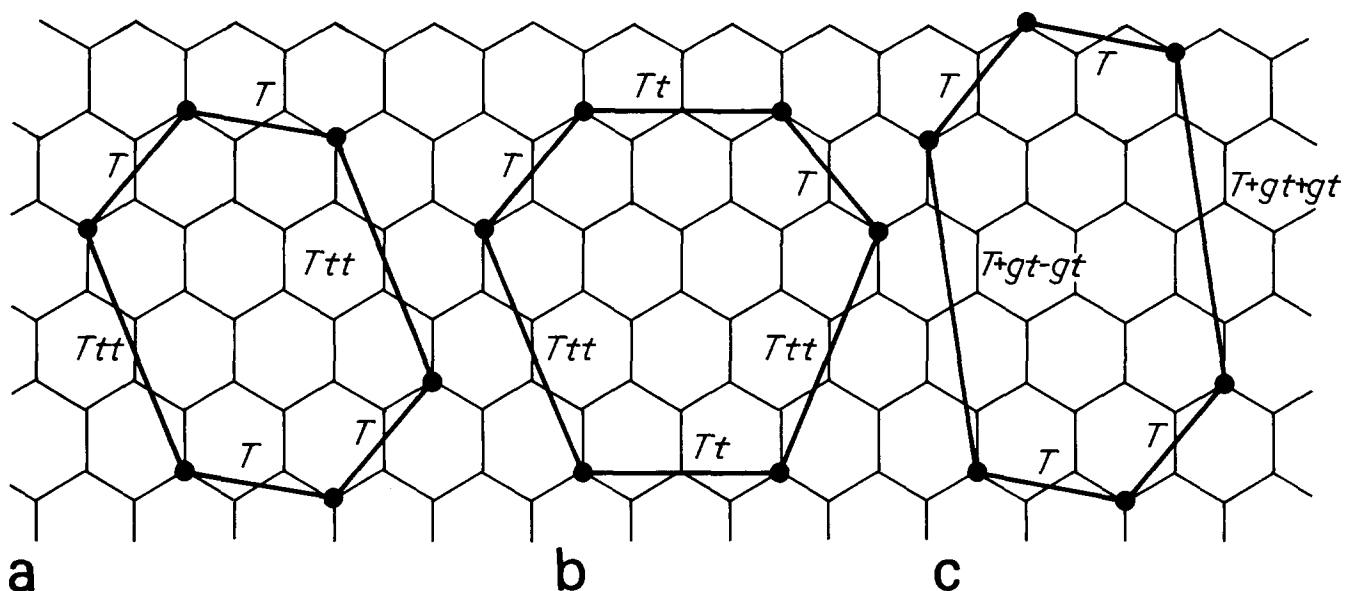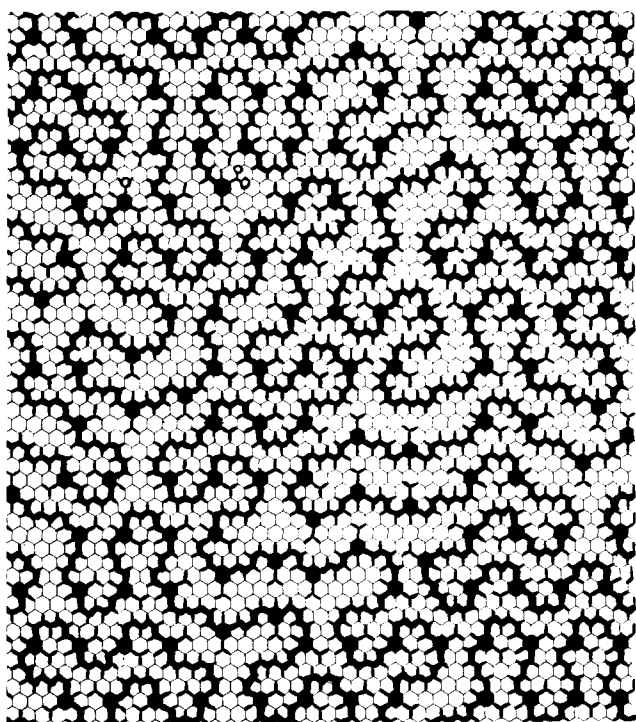
Figure 12 Larger SL polygons

Figure 13 Bulky polymer with **Figure 12b** as SL unit

Table 1 Physical parameters

N^a	$\langle R^2 \rangle^b$	$\langle D^2 \rangle^c$	$\langle D^2 \rangle / \langle R^2 \rangle$	$\langle T \rangle^d$	Log $\langle T \rangle$
32	114	16	0.14	0.14	−0.85
72	237	35	0.15	0.69	−0.16
112	350	53	0.15	1.59	0.20
180	459	87	0.19	4.56	0.66
264	622	123	0.20	12.0	1.08
336	824	157	0.19	22.0	1.34
448	1132	186	0.16	46.4	1.67

[a] N: Number of lattice points
[b] $\langle R^2 \rangle$: Mean squared end-to-end distance
[c] $\langle D^2 \rangle$: Mean squared radius of gyration
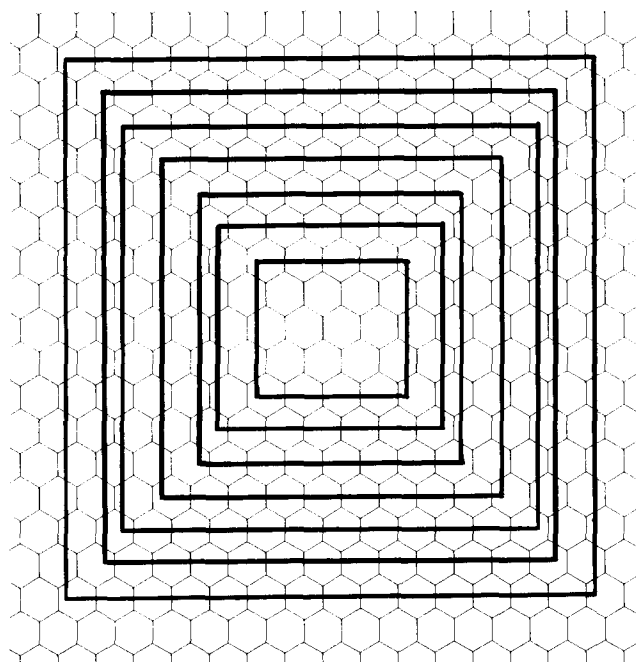[d] $\langle T \rangle$: Mean CPU time in seconds

Figure 14 Lattices used

of different size were chained a hundred times. In *Figure 14* the lattices are given. The distance between two lattice points is unity. Cyclic boundary conditions are applied. The results are given in *Table 1*. The mean square end-to-end distance $\langle R^2 \rangle$ can be described by

$$\langle R^2 \rangle = 2.52(6)^* N \tag{2}$$

The agreement between theory and experiment is very good. The constant $c1$ in the expression was determined by a least squares fit to the data. The standard deviation in the last decimal is given in parenthesis.

When the constant $c2$ is also refined, the fit does not improve significantly. This is quite remarkable and contradicts earlier RW computer simulations on two-dimensional lattices (see ref. 3) that produced a value 1.5
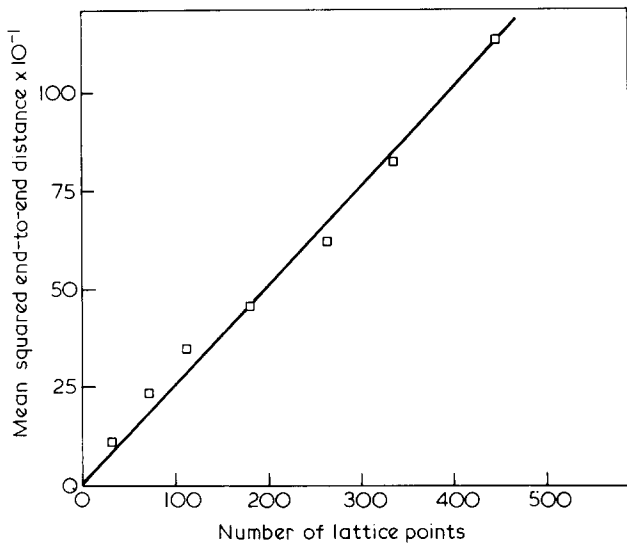
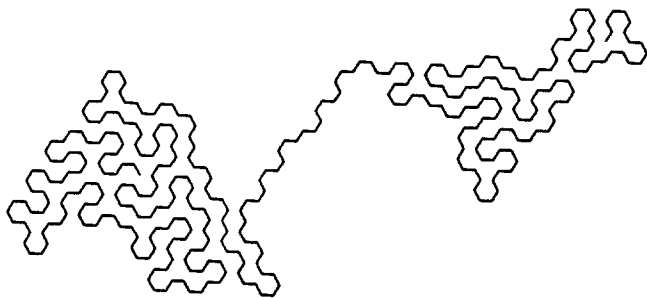Figure 15 $\langle R^2 \rangle$ as a function of N

a

Figure 16 Typical two-coil chain

for the constant $c2$. In *Figure 15* observed and calculated values are shown.

The reason for the proportionality between $\langle R^2 \rangle$ and N, a feature that random walk models lack, is the symmetry of the TS method, combined with the strong demand that every lattice point is on the chain. The construction of a self-avoiding random walk is asymmetric: there is an outspoken difference between the starting point and the end point. The starting point is fixed and being wrapped in by the growing chain. The end point moves and is on the outskirts of the model the larger time of the process. As soon as the moving endpoint folds back and enters the model, the changes are so large that a cul-de-sac is encountered and the walk is finished.

The TS method does not differentiate between the two extremes. Every point on the lattice has the same chance of becoming one of the extremes of the chain. This does not change during the process.

Also, random walks are known for their capability of closing in lattice points that cannot be reached any more. This is one of the reasons that the constant $c2$ for random walks will be larger than for methods like the TS method that do not show this handicap.

These essential differences make it difficult to compare the TS method with other model-generating methods.

Equation (2) is valid for the lattices given in *Figure 14*. For lattices of other shapes the constant $c1$ will undoubtedly have other values. To make $c1$ independent of the shape of the lattice and only dependent on the number of points N, every lattice tiling the plane,
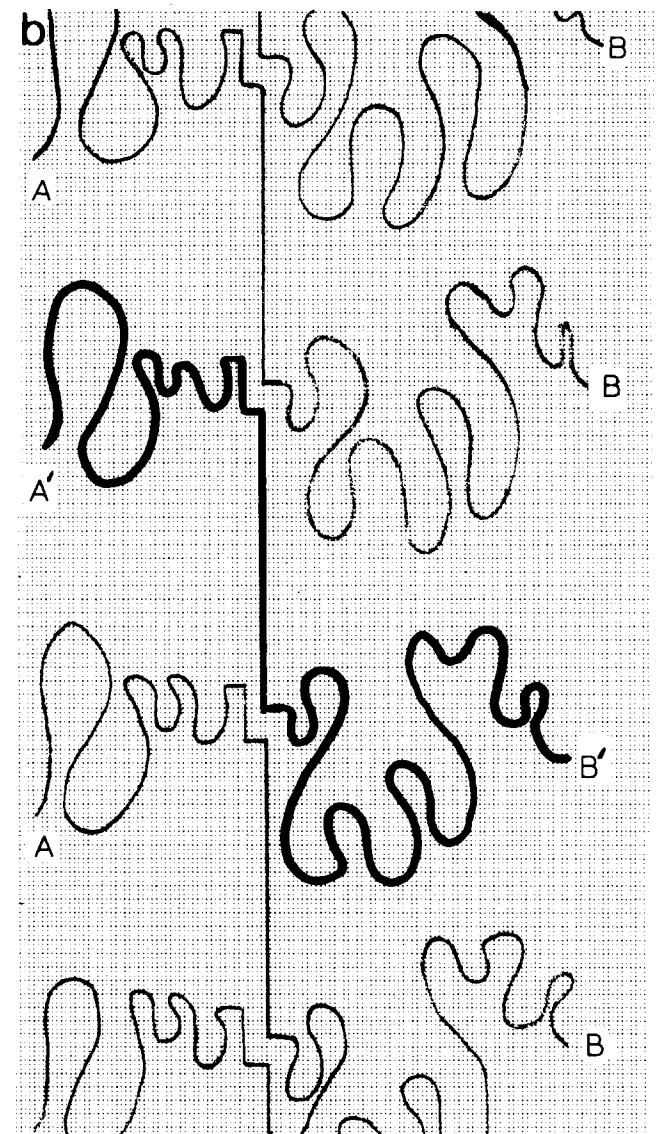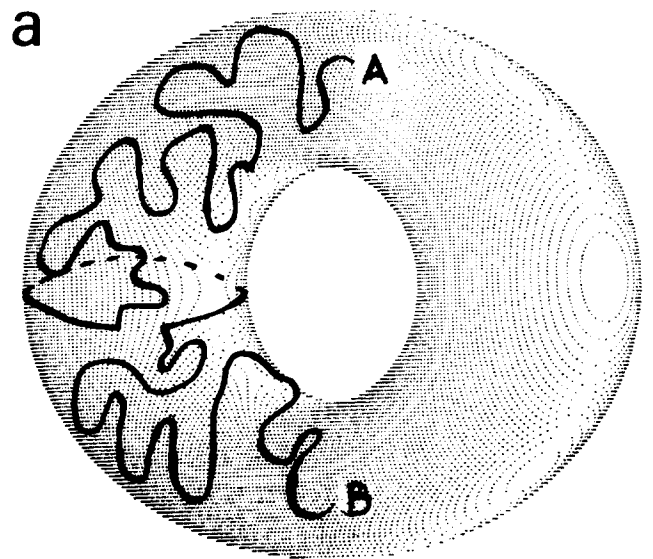

Figure 17 (a) Chain on a torus; (b) torus unfolded

consisting of N lattice points, must be investigated. The relative weight of every lattice can be calculated on, for instance, considerations of energy derived from the relative abundance of *gauche* conformations. Refinements like these fall outside the scope of this article.

Another quantity of interest is the radius of gyration D^2 (ref. 4). For unconstrained random walks this quantity is one sixth of the mean square end-to-end distance. In *Table 1* values of $\langle D^2 \rangle$ and the ratio $\langle D^2 \rangle / \langle R^2 \rangle$ for the different lattices are given.

DISCUSSION

Limits of the procedure

With the present algorithm the calculation time is approximately quadratic in N: the number of steps the procedure takes is $\propto N$ and the duration of one step is $\propto N/(N_c - 1)$. N_c is the coordination number of every lattice point. In *Table 1* the mean CPU time $\langle T \rangle$, in seconds, needed to generate a chain of length N is given. This time depends on the computer used (i.e. an Amdahl V7 B) and the compiler (IBM Fortran H-extended optimizing compiler). In general,

$$\log(\langle T \rangle) = k1 + k2*\log(N) \qquad (3)$$

The constants $k1$ and $k2$, for the lattices under discussion, were determined by a least squares fit to the data: $k1$ is $-4.2(1)$ and $k2$ is $2.20(7)$. Least-squares standard deviations in the last decimal are given in parentheses.

If we do not want to use more than one hour of CPU time for one chain, the maximum number of points in lattices as drawn in *Figure 14* is 3350. As one bond stands for 3 CH2-groups, this number corresponds to a molecular weight of 140 000.

For three-dimensional models the circumstances are generally more favourable in two ways: first, N_c is larger (in a subsequent paper we will show a three-dimensional model of polyethylene on a BCC lattice for which N_c is 8) and, secondly, one bond in the SL lattice will correspond to a larger number of atoms in TL (for the three-dimensional model of polyethylene, one bond in SL is 6 CH2 groups in TL). The implication is that models of polyethylene molecules with a molecular weight of 600 000 can be generated using one hour of CPU time.

The present version of CHAIN is written in Fortran. However, the whole process is based on bookkeeping rather than on arithmetic manipulations. It is therefore questionable whether in this case the optimizing compiler optimizes the correct steps. That is the reason that a version of the program was written in assembler language. This version is being tested now and an increase of speed of at least a factor 10 is to be expected.

No significant correlation between T and R could be detected. A typical value for the correlation coefficient C of these quantities, calculated as

$$C = \frac{\sum\limits_{k=1}^{100} (R_k^2 - \langle R^2 \rangle)(T_k - \langle T \rangle)}{\sum\limits_k (R_k^2 - \langle R^2 \rangle)^2 \sum\limits_k (T_k - \langle T \rangle)^2} 1/2 \qquad (4)$$

is 0.07.

Coiling

Some chains show features that can be described as 'coiling': the chain forms coils that are connected by thin threads (*Figure 16*). This is due to the dimension of the lattices. Three-dimensional models do not suffer from this abberation.

The cause of this coiling is the use of cyclic boundary conditions. The lattices shown in *Figure 14* can, because of the cyclic boundary conditions, be thought of as lying on the surface of a torus. When the chain has crossed the torus completely in one direction, as drawn in *Figure 17a*, this crossing prevents further contact between the two parts. This effect has no physical counterpart and does not occur in three-dimensional models.

ACKNOWLEDGEMENTS

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