'Domino' model of chain arrangement in bulk polymers

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A new model is presented that generates amorphous structures with linear chains filling up the space completely. The model is based on a simple concept that the space is filled up with elements containing chain segments that can be connected into chains according to the 'domino' game rules. Examples of model applications are shown.

(Keywords: amorphous structure; chain packing; chain conformation in bulk; 'domino' model; computer simulation)

INTRODUCTION

Interpretation of physical properties of bulk polymeric materials requires models of morphology on the molecular level. To be a fair representation of the actual geometry and packing of long-chain molecules in the space, such models have to satisfy a number of conditions related to single-chain statistics, local packing, dimensionality and macroscopic properties of the system. Consideration of all these conditions at the same time makes the problem difficult. This is why procedures for the generation of models of isolated macromolecular chains in space are well developed whereas the generation of spatial arrangements of macromolecules that fill up the space completely has not yet been solved satisfactorily. The main problem arises from the difficulties in accommodation of chains when they are packed to some density under obvious excluded-volume conditions but where occupation of nearly all of the available space is required.

The most standard model of chain systems in which the chemical details of the chain structure are omitted is the lattice model. A flexible polymer chain is represented in this model as a self-avoiding random walk on a periodic lattice. The walk is a succession of N steps subject to the condition that no lattice site may be visited more than once in the walk.

Attempts to generate condensed polymer systems using the lattice model have been made by application of various 'relaxation' processes to systems of free chains generated on a finite part of the chosen lattice. Several 'relaxation' mechanisms have been used, consisting of movements of one or a few chain segments[1-4] or based on reptation processes of the chains[5]. All known relaxation mechanisms can, however, operate successfully only when there are lattice sites still not occupied into which the relaxing structural units can move. Therefore models generated in this way cannot be completely filled up with chains.

Two methods of simulation have been reported that lead to generation of completely filled systems. The first introduces special 'relaxation' mechanisms based on chemical reactions[6,7] that have no realistic equivalence to physical relaxation processes. The second is based on the solution of the 'travelling salesman' problem and has been reported in application to two-dimensional models only[8].

This paper will present a method of chain system generation in which all of the chains are closely packed in three-dimensional space. The method is based on the simple assumption that the space is at first filled up completely with volume elements, each containing a chain segment passing through it, and then all elements are connected into chains. The excluded-volume condition is automatically satisfied in such a system because each element contains only one chain segment. The way in which the chains are built up can be compared to the rules of the 'domino' game, in which a proper position of a proper element has to be chosen to continue chain growth. The model will be presented for the simplest case of cubic unit elements.

Figure 1 illustrates the basic conceptual difference between the conventional lattice model and the 'domino model' in a two-dimensional simplification. In the first case, completed chains are introduced into the lattice one after another, while in the 'domino' model, space is *a priori* filled up by 'domino' elements, which are later connected into chains.

THE THREE-DIMENSIONAL 'DOMINO' MODEL

It will be demanded that the model satisfies the following conditions:

(1) Chains should be linear and randomly coiled in three-dimensional space.

(2) Chain segments should be locally packed under excluded-volume conditions.

(3) Chains should fill up the space completely.

(4) The system should become isotropic and homogeneous on a size level not much greater than the size of elemental chain segments.

To satisfy these conditions we first assume that the model is an aggregate of closely packed cubic elements, each containing chain segments passing through the element. The chain segment in the cubic cell consists of two subsegments connected in the centre of the cube. The subsegments can assume various orientations, remaining,

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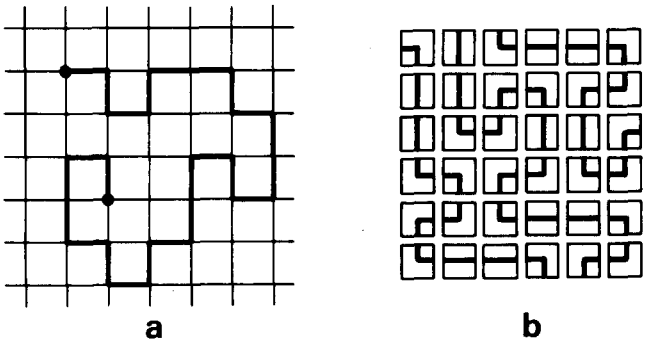


Figure 1 Schematic comparison of two types of chain conformation models: (a) conventional lattice model (completed chains are filled in); (b) 'domino' model (space completely filled by 'domino' elements, chains are built up according to 'domino' rules)

however, non-overlapping and always perpendicular to the cube faces. Each cubic cell ('domino' element) has in this way two chain connecting faces and four blank faces. The element defined in this way is shown schematically in *Figure 2a*.

Starting to connect the elements into chains, the computer program chooses at random the orientation of the first element. There are 15 possibilities for orientation if complete flexibility of the chains is assumed: three '*trans*' conformations in the three principal directions when the subsegments are collinear and 12 '*gauche*' conformations where the chain is bent within the cube. The possibilities of orientation of the next element adjacent to the first one are limited because only blank to blank faces and chain-connecting to chain-connecting faces can adjoin according to condition (2). The program again chooses the orientation of the element randomly but considers only the accessible cases. In general, the orientation of each element is chosen by consideration of the orientations of the six elements from the nearest neighbourhood. The sequence in which the elements are connected into chains has no influence on the structure if situations are omitted in which a new element has to adjoin more than three already positioned elements. These situations also have to be omitted if one would always like to find at least one acceptable position for the new element. Depending on the local situation created by already positioned elements, each newly considered element can (i) connect two already existing chains, (ii) propagate an existing chain or (iii) create a new chain. The positioned elements are assigned by an orientation code and by a chain number code.

We have used a special orientation code allowing us to save all information related to orientation of elements by means of one three-dimensional matrix $m(i, j, k)$ where i, j, k describe positions (coordinates) of the 'domino' elements in the model system. The orientation of each 'domino' element is first characterized by three natural numbers l_x, l_y and l_z which describe the presence and orientation of subsegments in directions x, y and z respectively. In *Table 1* we show the possible values of l_x chosen as an example. Other directions are characterized in an identical way. Using values of l_x, l_y and l_z, the orientation of each 'domino' element can be described by

$$m(i, j, k) = 100l_x + 10l_y + l_z \qquad (1)$$

A part of the system consisting of eight domino elements is shown in *Figure 2b*. The model can be expanded in all directions to sizes that are limited only by the capacity of the computer memory. A peculiar property of the model is that it is not necessary to introduce chain ends. The chains formed stick out at the faces of the model and the model as a whole can be regarded as cut out from a larger system. An example of a cross-section of the model with flexible chains can be seen in the first picture of *Figure 9*. A single chain taken from this model is shown in *Figure 3*.

SOME RESULTS

The amorphous state

Models of amorphous states of size 32^3 elements have been generated by choosing at random one of the possible orientations for each 'domino' element. Chain ends have not been introduced. As a result, all chains pass through

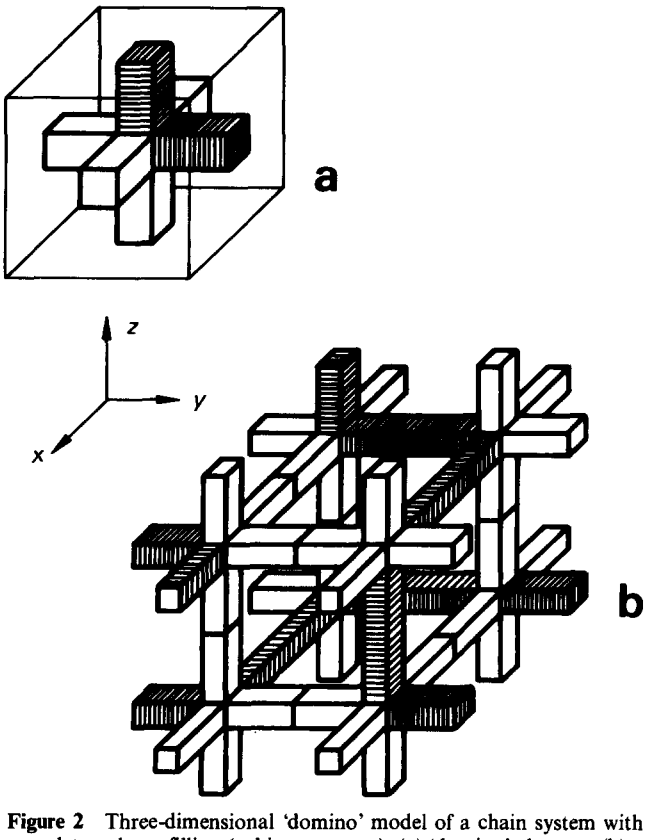
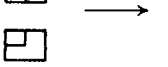


Figure 2 Three-dimensional 'domino' model of a chain system with complete volume filling (cubic symmetry): (a) 'domino' element; (b) a system consisting of eight elements

Table 1 Orientation code for one direction

l_x	Orientation	Graphical illustration
1	No subelements in x direction	
2	One subelement in negative x direction	
3	One subelement in positive x direction	
4	Two subelements in x direction (collinear)	
5	As in the case $l_x=2$ with chain end	
6	As in the case $l_x=3$ with chain end	

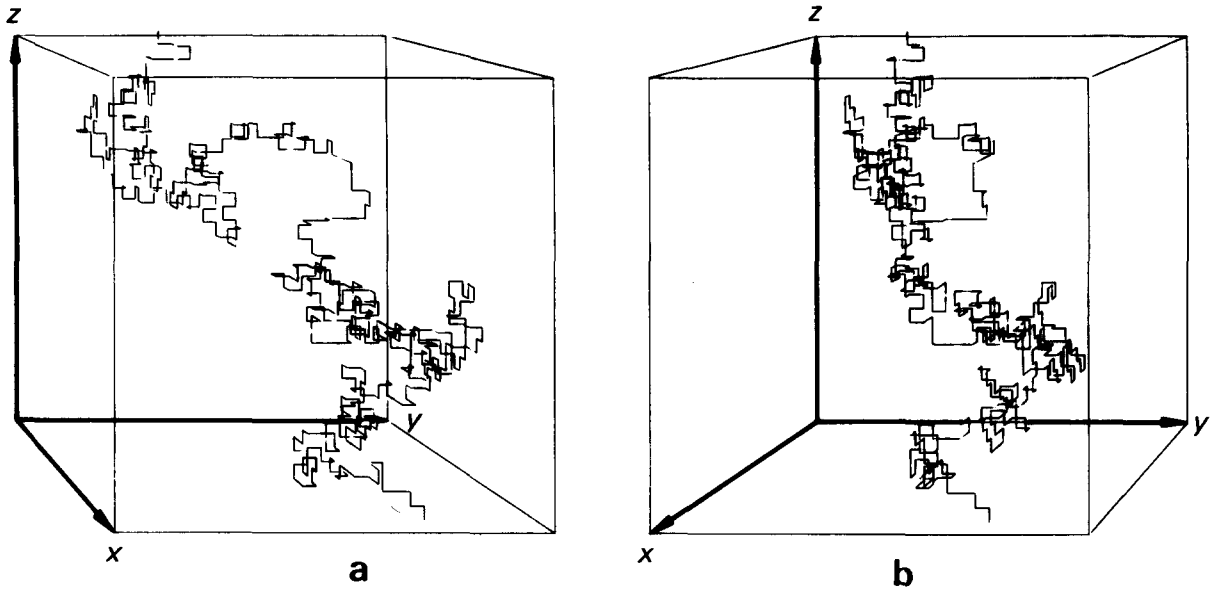


Figure 3 Example of a chain in a system generated according to 'domino' model: (a) and (b) two different side views

the model having their ends accidentally distributed at model faces and having accidental lengths within certain limits related to model size (the longest chains observed in our case were about 800 elements long).

Two quantities have been determined to characterize the properties of generated chains. The first is the mean-squared end-to-end distance of chain segments of length N between the ith and jth elements of the chain:

$$\langle R_N^2 \rangle = \langle (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \rangle \quad (2)$$

The second is the mean-squared radius of gyration of chain segments of length N:

$$\langle s_N^2 \rangle = \left\langle \sum_{k=i}^{j} [(x_s - x_k)^2 + (y_s - y_k)^2 + (z_s - z_k)^2]/N \right\rangle \quad (3)$$

where x_s, y_s, z_s are coordinates of the centre of gravity of the chain segment between elements i and j.

Results are shown in *Figure 4*. Both quantities show linear dependences with respect to N, giving

$$\langle R_N^2 \rangle = 1.62N \quad (4)$$

$$\langle s_N^2 \rangle = 0.26N \quad (5)$$

and indicating that Gaussian chains have been generated which are only slightly more expanded than random-walk chains on cubic five-choice lattices, for which dependences (4) and (5) should have coefficients of 1.5 and 0.25, respectively[9].

To characterize the orientational state and homogeneity of the generated system, the mean orientation fluctuation parameter has been determined:

$$\langle f \rangle = \left\langle \frac{2}{3} \left[\left(\frac{\bar{n} - n_x(V)}{\bar{n}} \right)^2 + \left(\frac{\bar{n} - n_y(V)}{\bar{n}} \right)^2 + \left(\frac{\bar{n} - n_z(V)}{\bar{n}} \right)^2 \right] \right\rangle \quad (6)$$

where $\bar{n}$ is the mean number of chain segments oriented in each direction in a completely isotropic system, $n_x(V)$, $n_y(V)$ and $n_z(V)$ are numbers of segments in a volume element V oriented in the x, y and z directions, respectively. The parameter $\langle f \rangle$ assumes the value 0 when the volume element V is isotropic and the value 1 when there exists perfect uniaxial orientation in the volume considered.

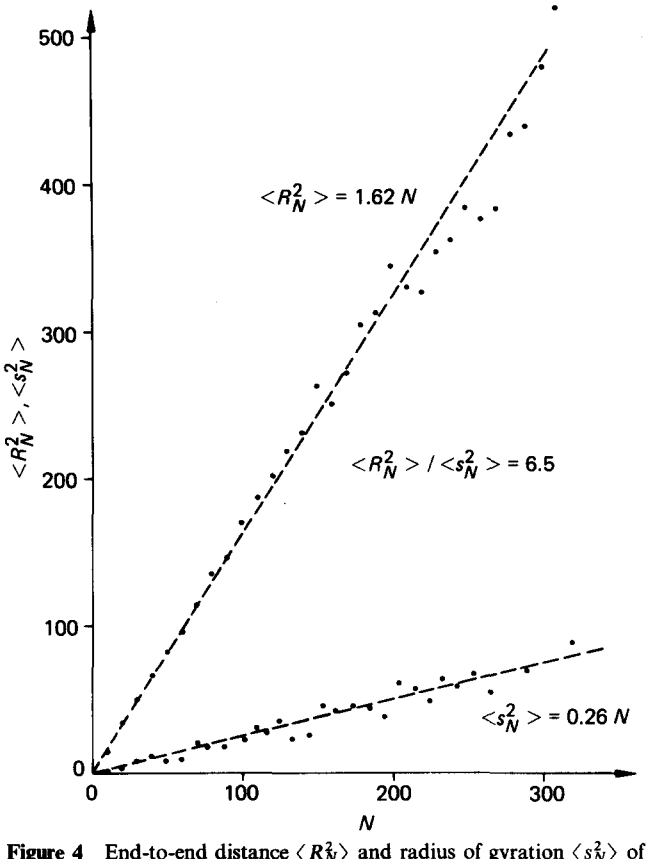


Figure 4 End-to-end distance $\langle R_N^2 \rangle$ and radius of gyration $\langle s_N^2 \rangle$ of chain segments of length N. Model size is 32^3 elements

In *Figure 5*, values of $\langle f \rangle$ are plotted as a function of the ratio V/V_0 (where V_0 is the volume of a single 'domino' element). Results show that on the small size scale, i.e. in volume elements smaller than about 100 'domino' elements, the system is heterogeneous because of non-negligible orientation fluctuations. Volume elements of sizes larger than $10^3 V_0$ can, however, be regarded as isotropic. This shows that the procedure of the 'domino' model generates isotropic systems with only local orientation fluctuations.

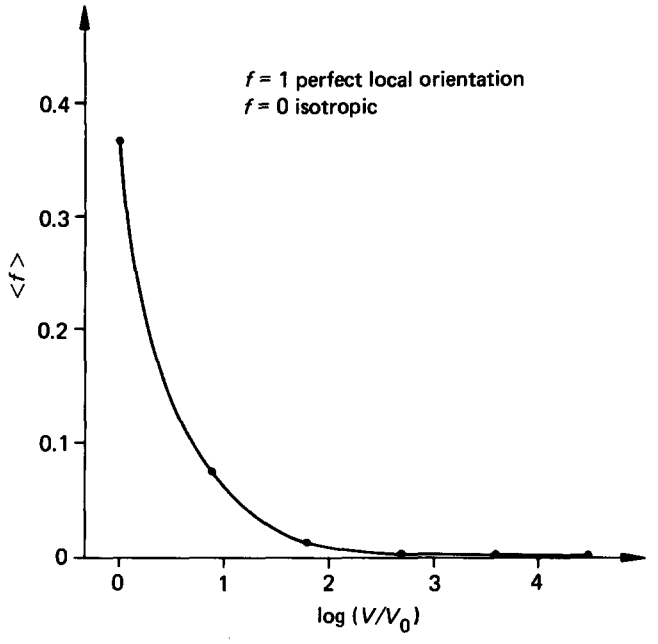


Figure 5 Mean orientation fluctuation parameter $\langle f \rangle$ as a function of the volume of the considered model parts

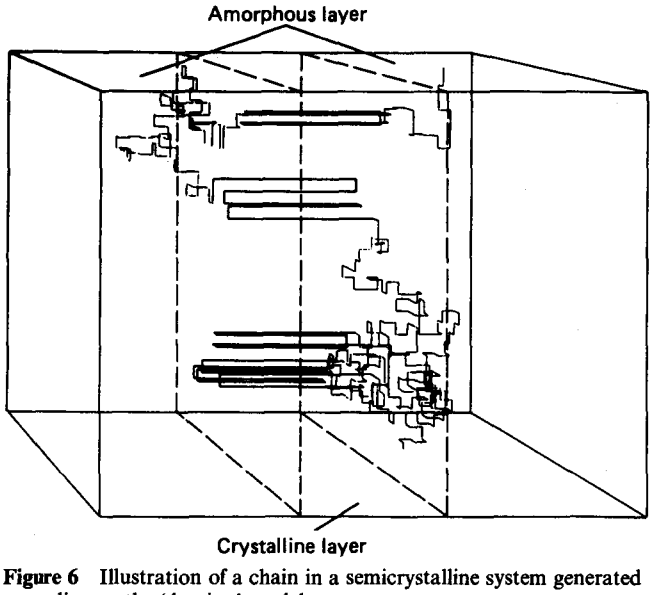


Figure 6 Illustration of a chain in a semicrystalline system generated according to the 'domino' model

Amorphous layer in semicrystalline system

The model can be used to simulate the structure of an amorphous phase adjacent to a crystalline lamella by introducing into the system a layer of 'domino' elements with chain segments perfectly oriented in the direction perpendicular to the layer surface. This layer will represent the crystalline phase and the amorphous structure can be generated in the remaining part of the model. An example of a single chain taken from such a model is shown in *Figure 6*. The chain passes many times through the crystalline layer, forming many adjacent re-entry loops and some longer loops immersed in the amorphous phase. *Figure 7* shows a distribution of chain flux along the direction perpendicular to the surface of the crystalline layer. The mean chain flux in the amorphous isotropic phase should fluctuate slightly around the value of one-third of the overall number of chains passing through the crystalline layer. This is observed in the amorphous phase generated, except for the minima in the vicinity close to the interface between crystalline and amorphous layers. The minima at the lamella surfaces are caused by the large number of adjacent re-entry folds. The distribution of chains around the crystalline layer is also characterized in *Figure 8* by the concentration distribution of chain elements belonging to chains that have passed through the crystalline lamella and have reached a distance z from the lamella surface. It is seen that the concentration of chain elements directly connected with the lamella decreases with the distance z from the lamella surface. This is a result of the possibility that chains coming out through the lamella surface can re-enter the crystalline phase, forming loops which, depending on their lengths, can reach only some limited distances from the lamella. The distribution shown in *Figure 8* is dependent on the lateral size of the amorphous layer. Therefore, the example presented here should be regarded as an illustration of the model application only. The problem of chain conformations in semicrystalline models will be discussed in another paper.

Systems with various molecular stiffness

Using lattice simulations, Yoon and Baumgartner[10] have recently observed a transition from ordered to disordered phases and vice versa when the ratio of probabilities of *'trans'* (collinear) p_t and *'gauche'* (transverse) p_g connections between successive chain segments is changed.

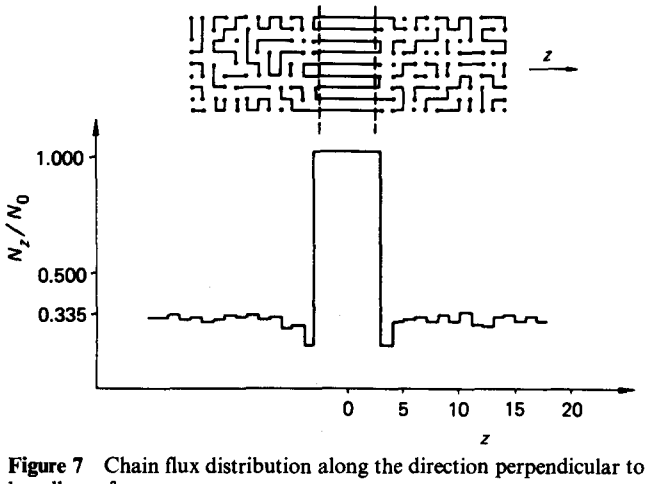


Figure 7 Chain flux distribution along the direction perpendicular to lamella surface

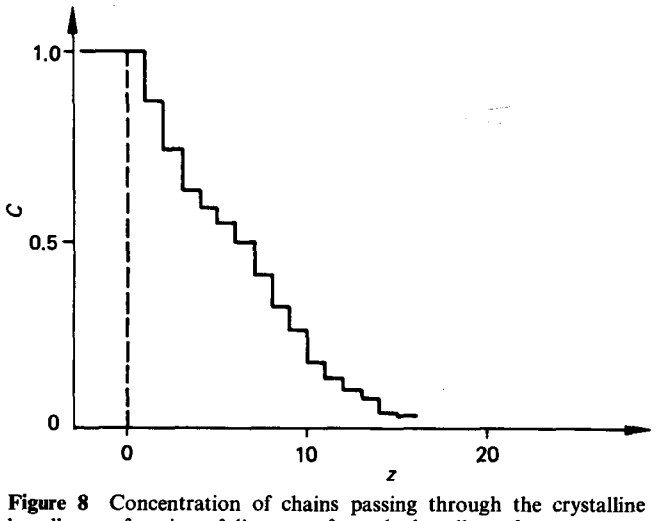


Figure 8 Concentration of chains passing through the crystalline lamella as a function of distance z from the lamella surface

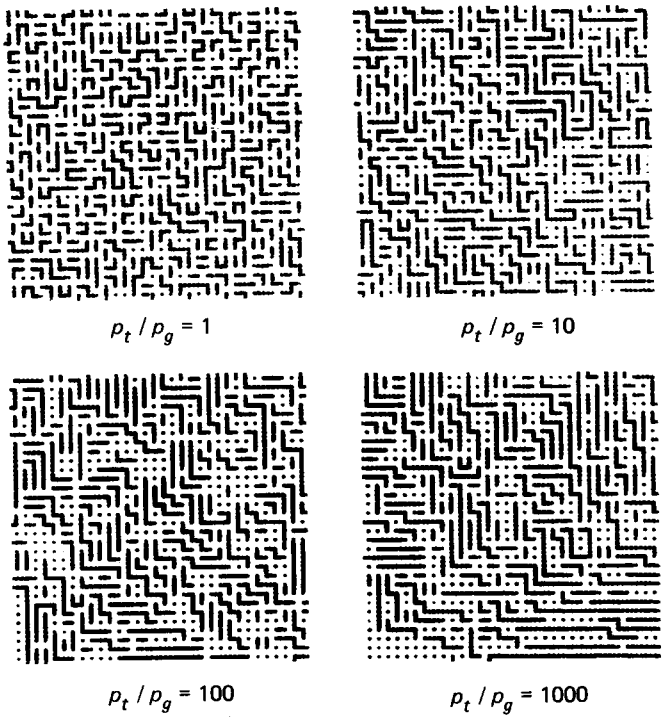


Figure 9 Illustration of an increase of local orientational order in systems with various probabilities of '*gauche*' and '*trans*' conformations

Using the 'domino' model we have also generated systems in which the ratio p_t/p_g was changed over a wide range. The orientation of elements in such models was sampled from accessible possibilities with respective weighting factors related to values of p_t and p_g. In *Figure 9*, examples of cross-sections through models calculated with various p_t/p_g ratios are shown. Qualitatively, an increasing local orientational order is observed when the value of p_t is much larger than p_g. In *Figure 10* the fraction of '*gauche*' bonds is plotted as a function of reduced temperature[10] $\tilde{T} = 1/\ln(p_t/p_g)$. The figure also shows this function for unperturbed chains on a cubic lattice[10]. Our results do not indicate any transition like that observed by Yoon and Baumgartner[10]. The dependence of g on $\tilde{T}$ obtained for the generated model systems is in our case similar to that predicted for unperturbed chains except for the fact that in our case the number of '*gauche*' conformations is always higher than that predicted for unperturbed chains or for completely flexible chains when $p_t = p_g$.

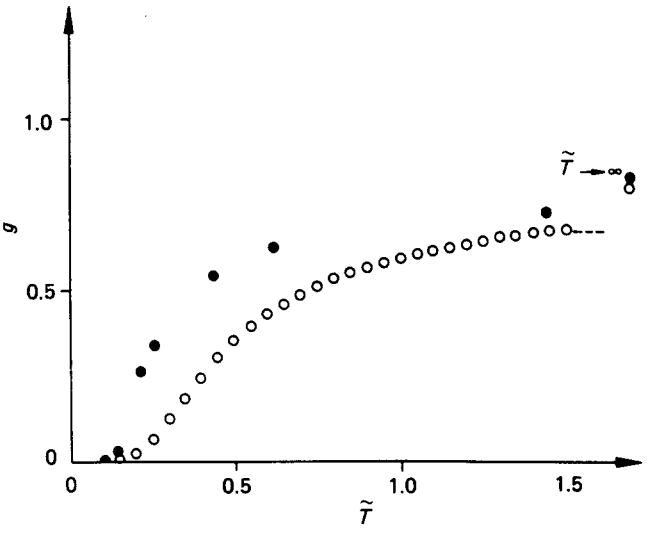


Figure 10 Fraction of '*gauche*' conformations as a function of reduced temperature in model systems (●) compared with dependences predicted for non-perturbed chains (○)

CONCLUSIONS

A new model has been presented that generates amorphous structures with linear chains filling up space completely. Analysis of segment distributions in the generated chains has indicated that nearly Gaussian type chains have been obtained. Application of the model to the amorphous layer in semicrystalline polymers and to simulation of polymer systems with variable stiffness have been presented as examples illustrating the possibilities of the model.

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