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Cooperative Relaxations in Condensed Macromolecular Systems. 1. A Model for Computer Simulation

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Received September 9, 1986

ABSTRACT: A microscopic model of cooperative relaxations in condensed macromolecular systems is proposed. The mechanism suggested consists in collective replacement of molecular subsegments within closed loops of motion. The model is applied to computer simulations of chain motions on a lattice with all sites occupied. Examples of computer experiments based on melting of regular structures with linear and ring chains are shown. Final isotropic amorphous systems that are completely filled with ideal randomly coiled chains have been obtained. Chain lengths were varied between 16 and 1024 chain segments.

Introduction

The molecular motion of polymer chains in the condensed state has been intensively studied for several decades both experimentally and theoretically. These studies have demonstrated that the properties of polymers concerning molecular mobility are very unusual and complicated. The problem is well reviewed in a number of papers (e.g., ref 1 and 2). The major factor governing the overall molecular motion of a polymer chain in a dense system is the effect of entanglements caused by mutual uncrossability of neighboring polymer chains.

The recent picture of diffusion in entangled polymer systems is dominated by the idea of reptation. In the reptation model originally developed by de Gennes,[3] the polymer chains move along their own contours among their neighbors like a snake would move through a set of fixed obstacles. Lateral motions are strongly impeded by the neighboring chains, which make a tubelike region surrounding the chain contour.[4,5] To escape from the tube the chain has to diffuse along its entire contour length.

Predictions of the reptation model have evoked much recent experimental work on polymer diffusion in the melt (reviewed in ref 2). Results obtained with various experimental techniques have confirmed that the translational diffusion coefficient of N-mer chains varies as $D \approx N^{-2}$ in agreement with the reptation prediction for linear chains.

The reptation model is less successful, however, in describing the motion of branched or ring molecules where other mechanisms of relaxation and diffusion are necessary to understand the dynamics of these systems.[6] The weakness of chain-motion pictures based on the reptation model is that the chain is essentially considered as taking place between fixed obstacles. An infinitesimally small renewal of chain shape can eventually occur when the neighboring chains reptate away as considered, for example, by Klein.[7] This process is, however, noncomparably slower than the reptation itself. As a consequence, mobility of branched or ring molecules will be considerably frozen, which is not in agreement with experimental observations.[6]

Polymer chain motions have also been studied by computer simulations. The reptation mechanism[12] or various "relaxation" processes consisting in movement of one or few segments inside the chain[8-11] have been used to move chains on a lattice. Reptation and all known relaxation mechanisms can, however, only operate successfully when there are lattice sites still not occupied into which the relaxing structural units can move. They are therefore nonapplicable to models in which space is completely filled with chains.

In this paper a model of molecular motion in condensed macromolecular systems is suggested, which is based on the cooperative movement of an assembly of molecular subsegments belonging to various neighboring chains. The essential idea of the model is illustrated in Figure 1, where three chains taking part in the cooperative movement are shown. The movement consists of two contributing mechanisms: the first is based on position exchange between chain elements belonging to two different chains being locally in immediate contact (areas marked in the figure by circles) and the second consists in translational movement of chain subsegments along the chain contour between subsequent position-exchanging areas. The first type of movement involves local shape changes in both chains taking part in a position exchange. This demands, however, special local configurational arrangements of adjacent chains. The example shown in Figure 1 assumes that there is a kink on one of chains which can be pulled in and replaced by a kink formed on the other chain (Figure 1b). The second type of movement is equivalent to local chain reptation. It is assumed that all moving elements constitute a closed loop and can be regarded as a cooperatively moving assembly. Within the moving loops, chains move along their chain contours and the motion is transferred from one chain to another by position-exchanging units. The directions of respective motions are marked in Figure 1 by arrows. As a result of this motion, each element in the loop shifts to a new position occupied before by another adjacent element also belonging to the loop. This means that the motion is performed by collective replacements within the loop and no additional volume is needed for such a rearrangement. It has been noticed during the preparation of this manuscript

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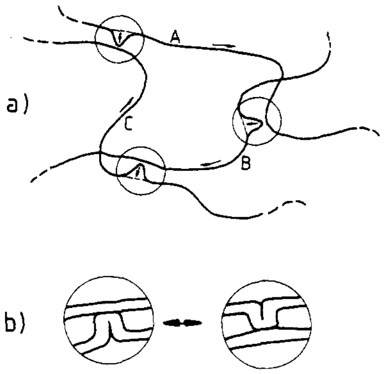

Figure 1. (a) Schematic illustration of the closed-loop motion of three chains (A, B, and C) with three areas of position exchange (circled). Arrows denote the direction of movement. (b) Magnification of the area of position exchange with the kink on one chain that is pulled in and simultaneously replaced by the kink formed on the other chain.

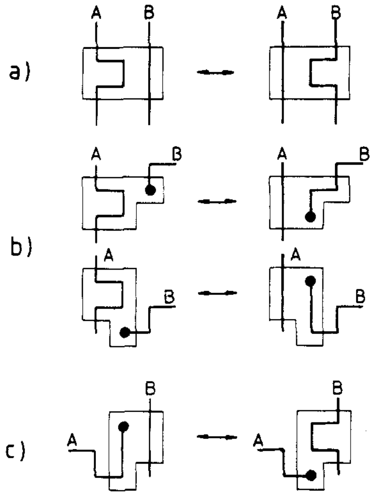

Figure 2. Examples of various rearrangements considered as position-exchanging areas on the lattice: (a) kink-to-kink transformation; (b) kink-to-chain end (two cases); (c) chain end-to-kink.

that the model described here has some conceptual similarities to the approach presented recently by Edwards and Vilgis.[13]

The model will be first introduced as it is applied to computer simulations. The analytical treatment will be presented in a subsequent paper.

Mobile Loops on a Lattice

We consider a condensed system of long linear chains of freely joined elements on a cubic lattice. Only topological regularity of the lattice is demanded. This means that the arrangement of sites which the chains pass through has the topology of a cubic lattice, but the interchain spacings can locally deviate from positions presumed in the regular lattice. The chains of N elements fill the lattice completely so that each lattice site is occupied.

In such a system we would like to perform chain motions according to the idea shown in Figure 1. We have to specify first, in detail, the local rearrangements that allow transfer of motion from one chain to another.

In Figure 2 the examples of position-exchanging local rearrangements are shown. In the first case (Figure 2a), the kink on chain A exchanges position with a part of chain B lying in closest adjacency and being locally parallel to the top segment of the kink. As a result, the kink on chain A is pulled in and is replaced by another kink formed now on chain B. In the second case (Figure 2b), the kink on chain A exchanges position with the end of chain B. Finally, in Figure 2c, the end of chain A exchanges position with adjacent chain B on which a new kink is formed. It is easy to imagine the case (not illustrated in Figure 2) in which two neighboring chain ends exchange their positions.

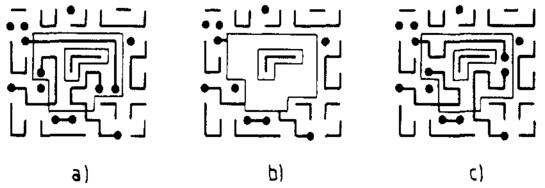

Figure 3. Cooperatively moving loop on a lattice (two-dimensional simplification). The state in (a) can be transformed to the state in (c) and vice versa. The empty area in (b) shows the area of mobile loop.

In the three-dimensional case, each kink or chain end can have more than one possibility to exchange position with other chains in the neighborhood.

The above rearrangements, when only locally considered, would change the number of elements in both chains. Chain A would become shorter and chain B longer, both by two elements. These length defects on both chains are, however, compensated by respective motions of chain segments between subsequent areas of position exchange so that, when the loop of movement is closed, all chains taking part in the rearrangement have exactly the same number of bonds as before but every chain element incorporated into the loop has been replaced along the loop.

An example of closed-loop rearrangement on the lattice is shown in Figure 3. There are three chains taking part in the rearrangement. The initial state shown in Figure 3a transforms to the state in Figure 3c. There are three position-exchanging rearrangements transferring the motion between three chains and closing the loop of motion. The area in which the movement takes place is left empty in Figure 3b, and only the nonmobile parts of the close-packed model are shown. The figure illustrates that the movement suggested here involves a collective rearrangement in part of the system without any changes in the neighborhood. Moreover, it does not need any explicitly introduced free volume in the form of empty lattice sites.

The spatial form of mobile loops is dependent on the structure of the system considered. In a three-dimensional random system of chains the loop can be assumed to have the form of a random walk ring because it consists of randomly coiled subchains.

It is clear that the probability of movements in the system with close-packed chains will depend on the concentration of places where position exchange between chain elements is possible. These places can be regarded as "bridges" between chains which allow the transfer of movement from one chain to the other, and the whole system can be regarded as a virtual random network consisting of mobility paths coinciding with chain contours and bridges through which the motion can be transferred between chains. For randomly coiled chains on a cubic lattice, the density of local conformatons in the form of kinks can be easily determined by calculating the probability of two adjacent gauche conformations with respective relative orientation. In our five-choice lattice with freely joined chains, the probability of single gauche conformation is $p = 0.8$; the probability of two adjacent gauche conformations along the chain is p^2. From all pairs of such elements only $^1/_4$ have relative orientations forming a kink, and thus the kink probability is $p_{\text{kink}} = 0.25p^2 = 0.16$. This

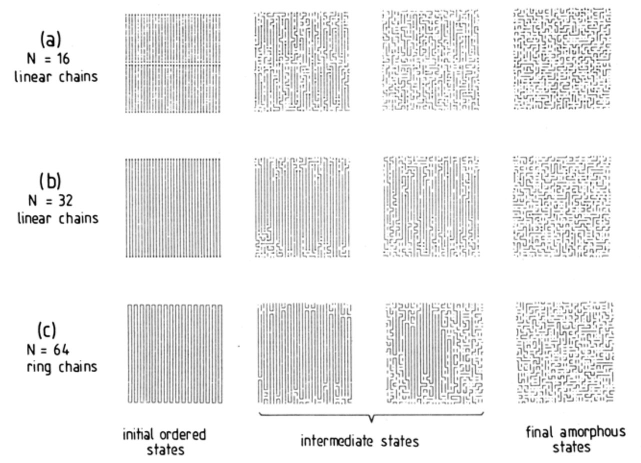

Figure 4. Examples of calculated structural changes during melting process in models with various chain length N: (a), (b) linear chains; (c) ring chains.

means that on the average we have a kink every 6–7 chain elements, making the virtual network of mobility paths very densely cross-linked. Additional bridges are introduced by chain ends, but their concentration is molecular weight dependent and is negligible for long molecules.

Examples of Computer Experiments

Calculations have been performed on three-dimensional lattice models of 32 lattice sites in each direction. Cyclic boundary conditions have been applied for both chains and mobile loops. The examples shown here start with regular (crystalline) chain structures in which chains are extended when shorter than the model size or folded regularly when longer, as can be seen in the first column of pictures in Figure 4. The formal description of the model used is the same as that presented for the "domino model".[14] The chains have been regarded as consisting of elementary units (domino elements), each including one lattice site with the chain segment passing through it. Each unit in the model has been marked by the number of the chain to which it belongs and by the orientation code as described in the former paper.[14]

Results presented in this paper can be regarded as being obtained for systems at infinitely high temperature because no limits have been imposed on the length of mobile loops. For each loop the motion has been initialized at a randomly chosen model element element and continued until the starting point has been found by the mobility path. This results in very broad distributions of loop lengths. The problem of loop-length distribution and its relation to the structure and temperature of the system will be considered separately in another paper.

Mobility paths have been searched according to the following rules: (1) To initialize a motion an imaginary searching point is positioned at random on an element of the system (monomer unit on a chain). (2) The point is moved in a randomly chosen direction along the chain, searching for a kink or chain end. (3) If a kink or chain end is found, the possibilities for position exchange with neighboring chains are examined (compare Figure 2). (4) One of the accessible possibilities is then chosen at random, and a respective position exchange is performed. (5) At the position exchange, the searching point is transferred to an element on another chain and the searching procedure according to the above rules is continued, starting again at (2). (6) The loop is closed when the searching point meets the starting point.

In Figure 4, examples of structure changes are shown for model systems with monodisperse chains. We present here cross sections through model systems in which only parts of chains lying in the cross-section plane are visible. Each chain element shown goes out of the cross-section plane at its ends unless it ends with the thick point, indicating the real chain end. Thin points indicate chains passing through the plane. The molecular weight in various model systems was varied between 16 and 1024 monomer units. The last example in Figure 4 shows the case of ring molecules having a length of 64 units.

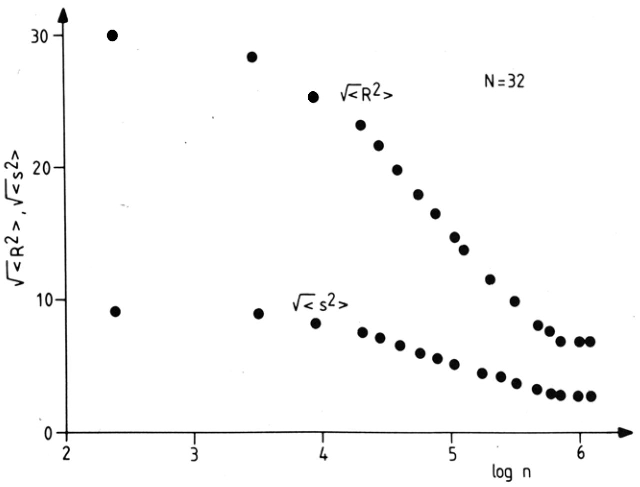

Figure 5. Example of calculated time dependences of mean values of end-to-end distance and radius of gyration during the melting process in the model with linear chains of length N = 32.

In all cases, when close-loop motions are performed, the regular initial structures transform to the molten isotropic amorphous state. During this melting process various structure-characterizing parameters have been determined as a function of time. As a measure of time the number of computer runs (n) searching for mobile loops is assumed. Only successful runs contribute, however, to structural changes in the system.

To observe changes of molecular dimensions we have calculated the mean-square end-to-end distance $\langle R^2\rangle$ and the mean-square radius of gyration $\langle s^2\rangle$. An example of changes in these parameters is shown in Figure 5 for linear chains of length 32. It is observed that as the melting process proceeds the chains become coiled, reaching some final mean values of end-to-end distance and radius of gyration. These values can be regarded as characteristic for the amorphous state of the model.

In Figure 6 the final $\langle R^2\rangle$ and $\langle s^2\rangle$ values are plotted as a function of chain length and indicate a linear dependence characteristic for randomly coiled chains. The ratio $\langle R^2\rangle/\langle s^2\rangle$ is close to six for all chain lengths, as is expected for Gaussian chains.[15]

The comparison of linear and ring molecules of length 64 also shows that the ratio of the radii of gyration of both types of chains is equal to two, as the theory predicts.[15]

Orientation changes in models with various molecular weights have been observed by determining the order parameter defined for the chains in a cubic lattice as

$$\langle f\rangle = \left\langle \frac{3}{2}\left[\left(\frac{\bar{n}-n_x}{\bar{n}}\right)^2 + \left(\frac{\bar{n}-n_y}{\bar{n}}\right)^2 + \left(\frac{\bar{n}-n_z}{\bar{n}}\right)^2\right]\right\rangle \tag{1}$$

where $\bar{n}$ is the mean number of chain segments oriented in each direction in a completely isotropic system and n_x, and n_y, n_z are the numbers of segments oriented in the x, y, and z directions, respectively. The order parameter so defined assumes a value of one for the system with perfect

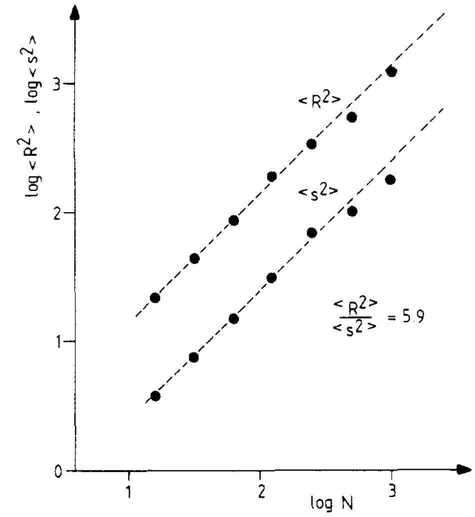

Figure 6. Chain length dependence of $\langle R^2 \rangle$ and $\langle s^2 \rangle$ determined for final amorphous isotropic states of models.

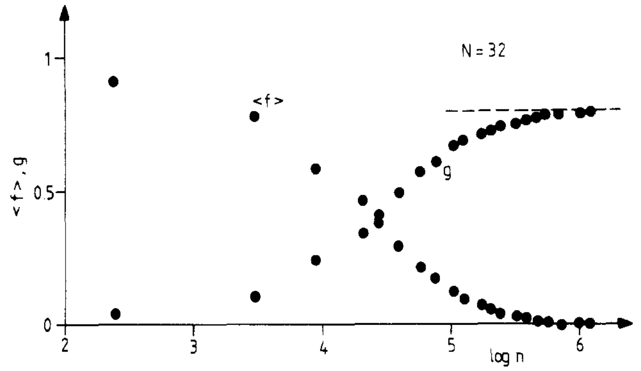

Figure 7. Changes in the orientation factor $\langle f \rangle$ and the fraction of gauche conformations (g) with time during the transformation of the model with $N = 32$ from the perfectly oriented state to the isotropic state.

uniaxial orientation and is zero for a completely isotropic system. Exemplary results shown in Figure 7 for chains of length 32 indicate that the initial perfectly oriented system of chains transforms into a completely isotropic form as already qualitatively demonstrated in Figure 4.

The conformational states of chains in the models have been characterized by determining the number of elements having trans (collinear) and gauche (transversal) conformations. For chains of length $N = 32$, the fraction of elements with gauche conformation ($g = n_g/M$, where M is the overall number of elements in the model system) is plotted as a function of time in Figure 7. It changes from zero for the initially completely extended chains to the asymptotic value of 0.8 for the final state of the model when the freely joined chains become randomly coiled.

Conclusions

We have shown in this paper that the new model suggested is able to cooperatively move polymer chains from a completely ordered state to the amorphous state. An interesting feature of the demonstrated model is that the motion does not need any explicitly introduced free lattice sites and the chains easily and cooperatively renew their shapes as one would intuitively expect in real polymer systems. This allows, for example, movement of ring molecules.

All parameters determined for the final state of the model systems show that isotropic amorphous states with ideal Gaussian chains have been achieved. This result agrees very well with chain conformation characteristics obtained by small-angle neutron scattering in bulk polymers[16,17] and demonstrates again the flexible chains in condensed amorphous systems are better described by the ideal random coil model than by the self-avoiding walks model.

Acknowledgment. I am grateful to Prof. E. W. Fischer for helpful discussions.

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