A Monte Carlo Simulation of a Knotted Linear Chain System as an Elementary Network Fragment

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Summary: We present the results of the Monte Carlo simulations of the dynamics of the linear chain system. The chains were constructed on a simple cubic lattice. The simulations were carried out by means of the classical Metropolis sampling method with the excluded volume effect present. No other interactions were introduced into the system (athermal polymer case). The linear chains in the system were constructed in such a way that there were knots at certain positions. Also, some chains were threaded through the knots forming the topological constraints in the system. The system under consideration underwent a series of micromodifications during the simulation run. Then the trajectory was analysed and the dynamics of the system was described by means of the autocorrelation functions. The short-time dynamics enabled us to investigate whether or not the knotted constraints affect the local dynamics of the chains. Also the long-time dynamics of the system can be useful in the characterizations of the dynamical properties of the fragments of the networks.

Keywords: knotted chains; lattice models; Monte Carlo method; polymer dynamics; polymer networks

Introduction

Polymer networks are systems of mutually connected macromolecules that have some specific physicochemical properties originating from the specific topology of the given material.[1] The macromolecules forming the network are usually jointed by chemical bonds between neighbouring chains. Besides this type of network one can find systems that behave as a network in the sense of their physical properties, but the system consists of macromolecular chains connected with other neighbouring chains by topological constraints, and therefore it can be treated as a polymer system featuring most of the properties of a network.[2-4]

The aim of this study is to analyse the stability of such topological connections in view of the dynamics of the system. The study of such collective motion of polymer chains seems to be interesting.[5-6] Here, we used a model developed previously for simulation of various properties of polymer chains and their systems. As a topological constraint in this model we

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have chosen simple knots. One can expect that the presence of knots would change the properties of the system towards those of network, at least on the short-time scale.

The Model and the Algorithm

We studied the simplest topological constraints, namely simple trefoil knots.[7] The knot, when embedded in the neighbouring chain, can form the stable topological constraint. In the case of many chains connected "topologically" a network-like system is formed.[2-3, 8] We analysed the behaviour of one and two-knotted linear chains. The knots consisted of 28 beads each. For each case we simulated the knots which were connected (or not) with another linear chain. Such a case enables one to determine the differences in the dynamics of the system for both cases. Figure 1 presents the topologies of the systems studied.

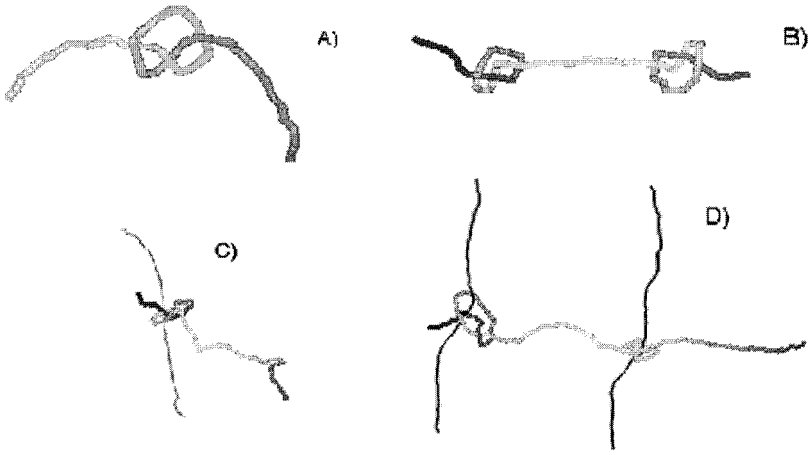


Fig. 1. Schematic representation of the systems studied. Linear chain with a single knot (A), linear chain with two knots (B), linear chain with one knot and with a threaded chain (C), linear chain with two knots with two threaded chains (D). Pictures taken from the simulations.

The model chains were built on a simple cubic lattice.[8-9] The chain had volume, i.e., it could not cross itself. No long-distance attractive potential or local stiffness was introduced into the model. The knots were constructed on the linear chain consisting of N beads so that they formed tight loops. We studied the following systems: a chain with one knot (model A), a chain with two knots (model B), a chain with one knot and with a second chain threaded through a loop formed by the knot (model C), and a chain with two knots and with two chains, each

threaded through a different knot (model *D*). The topology of chains in all models under consideration can be seen in Figure 1. The length of chains was varied from $N = 60$ to $N = 150$ beads.

We used the classical Monte Carlo algorithm based on the Metropolis scheme. In this algorithm the set of local micromodifications was used in order to sample conformational space.[8-9] The set of elementary motions consisted of one-bead motion, two-bead motion, two-bead crankshaft motion and end of chain reorientations. A new conformation of a chain chosen at random was accepted due to geometrical constraints and excluded volume.

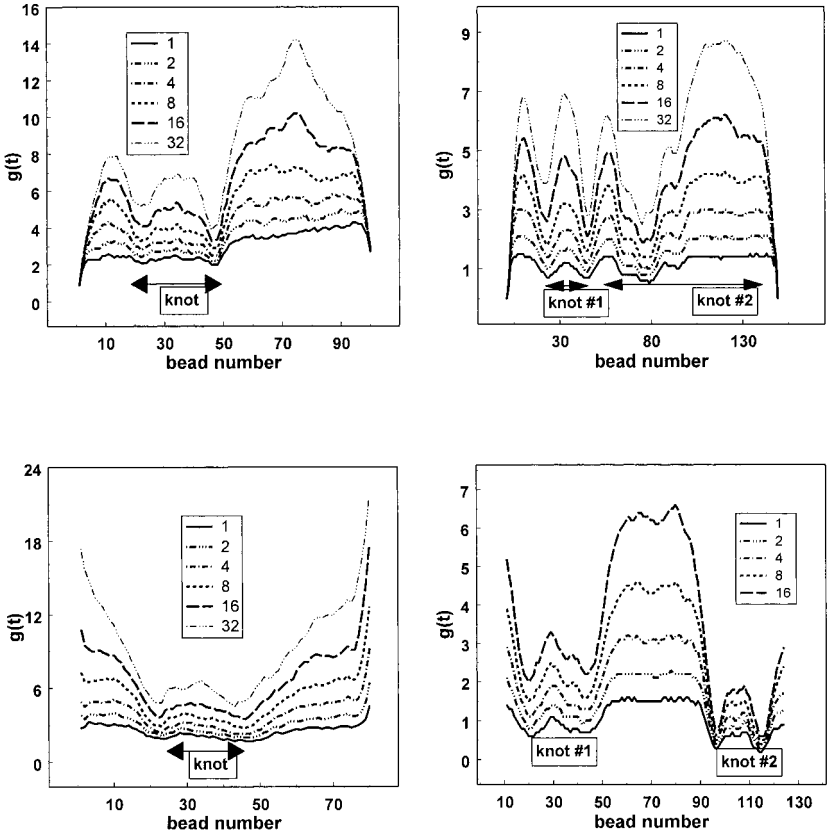
Results and Discussion

The dynamic behaviour of the model system can be studied by the means of the autocorrelation functions.[8-9] The single bead autocorrelation function *g(t)* is usually defined as follows:

$$g(\Delta t) = \left\langle [\mathbf{r}_i(t+\Delta t) - \mathbf{r}_i(t)]^2 \right\rangle \quad (1)$$

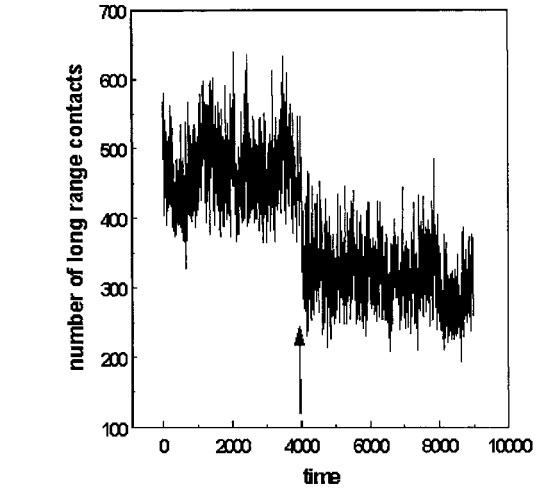
where $\boldsymbol{r}_i$ are coordinates of i^{th} polymer bead at times t and $t+\Delta t$ respectively. We have chosen rather small Δt because the process of disentanglement is relatively fast and one should be able to investigate the dynamics of the system at a short time scale.[10]

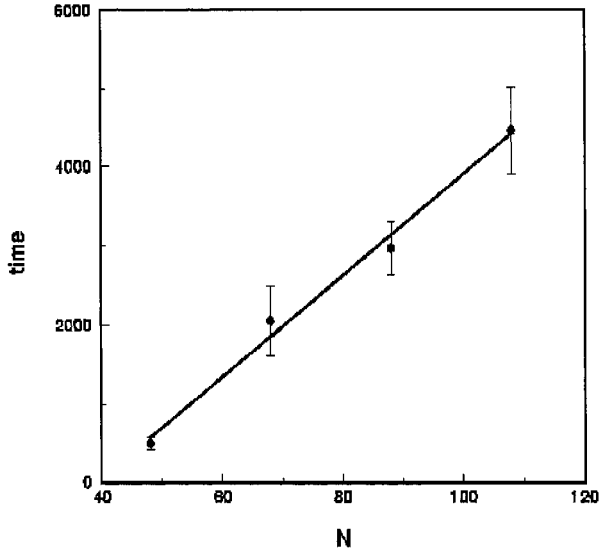
Figures 2-5 present the autocorrelation function versus the bead number for all systems under consideration. In all cases the chain with knots had both ends fixed; end fixation prevented disentanglement, which enables one to observe the system for sufficiently long time. It can be seen that some residues express low mobility: these are the regions of the "entrance" to the knot. This is visible in the region denoted as "knot #2" in Fig.2. However, the knot itself can be mobile, *i.e.*, it can "diffuse" along the chain, as can be observed in Fig.3 (knot #2). The arrow shows the region in which the knot #2 was present during the simulation. It is interesting that the beads inside the knot execute some motion, in contrast to those located at the "entrance" points. This is in very good agreement with the study of Saitta *et al.* who found that the greatest strain energy is located in the "entrance" points.[11] The presence of the threaded chains fixes the position of the knot and strongly hinders the mobility of the entrance points. The entrance points of knots are again almost immobile. This can be seen in Figs. 4-5.



Figs. 2-5. Autocorrelation function of a single bead *g(t)* as a function of the residue number *i*. Model *A* (upper left), *B* (upper right), *C* (lower left) and *D* (lower right). Time is given in insets.

Full disentanglement of a pair of chains takes place quite a long time after a knot is disentangled. The time of disentanglement can be estimated from the analysis of the total number of segment-segment contacts. Fig.6 presents the changes in number of contacts (first and second neighbours) with time. One can observe that the time of disentanglement if visible on this flowchart: the number of contacts decreases rapidly at the moment of disentanglement. In Fig.7 we present the dependence of the mean time of disentanglement on the length of chain. This dependence is linear, at least for short chains $\tau \sim N$.





Figs. 6-7. The number of contacts versus time (top). The mean time of disentanglement versus the number of segments (bottom), the standard errors are shown. The case of the model A.

Knotted chain systems seem to be a good approximation for topological networks. The results of Monte Carlo simulations showed that the presence of knots could be detected by the analysis of the dynamics of the model system. Moreover, the process of disentanglement of the knots

can be observed by monitoring the number of long-range polymer-polymer contacts. The time of disentanglement of the single trefoil-type knot was found to be proportional to the length of the chain.

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