Monte Carlo Simulations of Star-Branched Polymers in a Network of Obstacles

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SUMMARY: A simple model of branched polymers in space confined between two parallel plates is developed. Star-branched polymer molecules are built on a simple cubic lattice with excluded volume and no attractive interactions. A single star molecule is immersed in a network of irregularly dispersed linear rod-like obstacles. The classical Monte Carlo Metropolis sampling algorithm is employed in the simulation. The aim of this study is to determine the effects of changes in dynamic properties of the star-branched polymer as functions of the length of the molecule and the concentration of obstacles. Also the mechanism of motion of the polymer is discussed.

Introduction

Polymers confined in a network of obstacles and located between two plates separated by a distance comparable with chain dimensions are the subject of interest because of their practical significance (e.g., in liquid crystals, biological systems)[1)] as well as from a theoretical point of view. Theoretical considerations concerning the influence of the size and shape of confined polymer systems have recently been published[2,3)]. Also a system of linear chains confined between plates and immersed in a network of obstacles has been studied recently.[1)] The presence of a network of obstacles strongly affects the dynamics of such systems. In order to find out the dependence of the dynamics of star-branched polymer molecules on the size of the molecules, as well as on the concentration of obstacles, we have performed computer simulations over a wide range of parameters. Our goal was to see whether or not some interesting dynamic properties will develop with variation of the parameters. The study would also allow one to estimate the mechanism of motion of the macromolecule.

The Model

In our simulations we have employed a star polymer molecule with f=3 arms of equal length, n, emanating from a common origin called a branching point. The chains were constructed on a simple cubic lattice with excluded volume.[5)] The system was athermal, i.e., no long-range

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attractive and no local potentials were present. Hence, our model simulates good solvent conditions.

The simulations were made for a series of chain lengths. The polymer chains were located between the two impenetrable plates. The distance between the plates, d, was 5 lattice units. The periodic boundary conditions were applied in both the x and y directions. The z-axis was perpendicular to the plates. The system was also filled with a network of impenetrable rods (obstacles), occupying the space between the plates and situated parallel to z-axis. The rods were distributed in the system at random, provided any two of them are more than one lattice unit apart. The ratio of the number of lattice sites occupied by rods to the total number of lattice sites in the system was denoted as the rod concentration, φ.

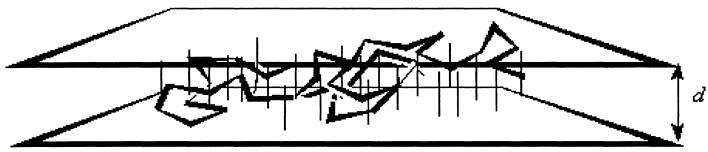

Fig. 1: Schematic representation of the model.

We used the classical Metropolis scheme in order to sample efficiently the configurational space and to calculate parameters describing the polymer size, shape, and dynamic properties. The initial configuration of a model chain underwent a series of local micro modifications where positions of a few beads (segments) were changed randomly. It was proved that a proper set of such modifications allows a chain to visit any point in the phase space. We used a set of motions, which was successfully used previously for star-branched chains - a detailed description of the elementary motions was given elsewhere[5].

Results and Discussion

We have performed a series of simulations for n = 5, 10, 17, 34, 67, 99 and 134 at a constant concentration of rods (φ=0.05). The total length of the chains was N=3(n-1)+1. Some simulations were performed for various φ (up to 0.2) at a constant chain length N=49.

The short-time dynamics characterizes the relaxation processes within the chain. The longest relaxation times, τ, were calculated from the center-to-end vector autocorrelation function. The relaxation processes are strongly depended on the chain length according to the relation $\tau \sim N^{\alpha}$. We have found that α to be 3.5±0.2, a value very close to the value observed in polymer melts (α=3.4).[6)]

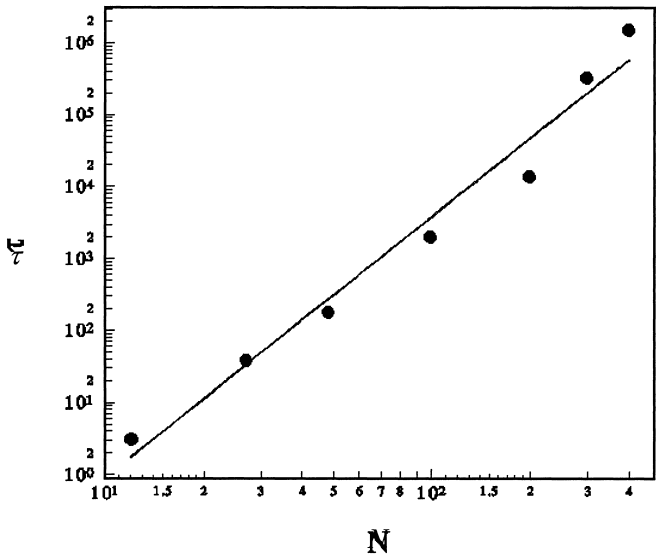

Fig. 2: Plot of the longest relaxation time τ as a function of chain length N.

The diffusion coefficient, D, (in xy projection) is defined according to Einstein's relation as $D=g_{cm}(t)/4t$ for sufficiently long times, where g_{cm} is the center-of-mass autocorrelation function. It is interesting, that the log-log plot (Fig. 3) is nonlinear. The curvature of the plot for longer chains suggests that an arm retraction mechanism of motion is present, as has been suggested.[7-9)]

The influence of the concentration of rods on chain diffusion is shown in Fig. 4. These are the results obtained for chains consisting of three arms of n=17 beads.

The variation of φ from 0 to 0.2 changes D by two orders of magnitude, showing the strong effect of the network of obstacles on the dynamics of macromolecules, even for relatively

small value of φ. A small concentration of obstacles causes a dramatic change in the mobility of chains: φ=0.05 slows the diffusion process down by about a factor of 3; φ=0.10 causes a reduction in D by about one order of magnitude.

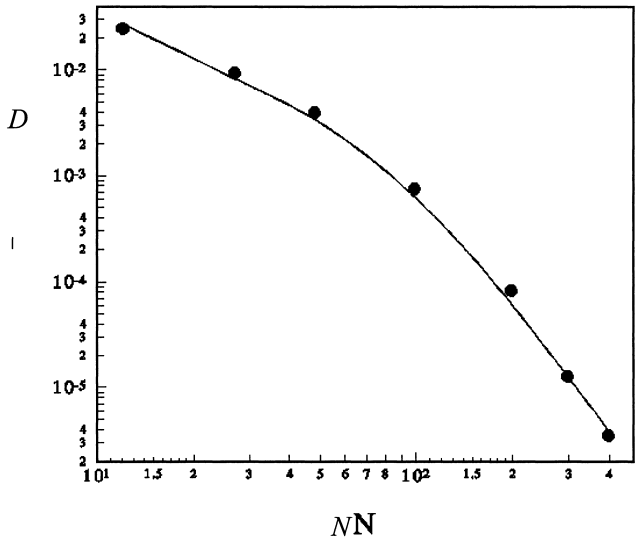

Fig. 3: Plot of the diffusion coefficient, D, as a function on chain length, N.

Concluding, one can state that the present model can enable investigations into the mechanism of motion of polymer chains confined in a specific environment to be carried out. The results obtained indicate that further simulations in that field could answer questions concerning the mechanism of chain motion.

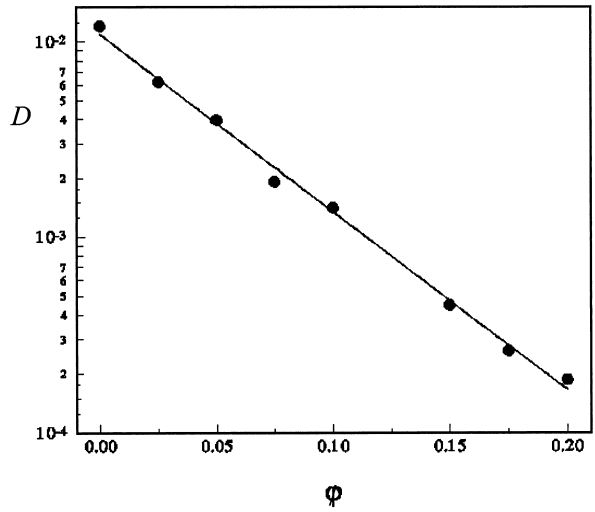

Fig. 4: Plot of the diffusion coefficient, D, as a function of concentration of rods, φ, for chain length N=49.

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