Properties of Star-Branched Polymer Chains. Application of the Replica Exchange Monte Carlo Method

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ABSTRACT: A simplified model of the star-branched and linear polymers was studied by the means of the computer simulations. The model chains were built on a simple cubic lattice forming star-branched polymers consisting of $f = 3$ arms of equal lengths. The simulations were carried out in a wide range of temperatures—from a random coil to a collapsed globule regime. The replica exchange Monte Carlo method was used for calculation of properties of the model system. The detailed comparison of this new method with the classical Metropolis scheme, which uses simulated annealing. It was shown that the Metropolis algorithm is correct for high temperatures. In the transition region and below the transition temperature the results obtained by the two methods differ significantly. The replica exchange technique finds lower energy states than the other method. The temperature of the coil−globule transition calculated using the RE algorithm is usually slightly shifted toward lower temperatures. The differences increase moderately with length of the chain and with its stiffness. The features of the transition do not depend on the simulation method although it is more rapid for the replica exchange simulations.

Introduction

A flexible homopolymer chain changes its size with the temperature or with the solvent conditions.[1,2] At high temperatures (or in good solvent conditions), it behaves like an extended random coil: its size parameters like the mean-square radius of gyration and mensquare end-to-end distance scale as $N^{1.2}$. The annealing of the system leads to the decreasing of the size of a polymer coil and at the Θ temperature the size of the chain without the excluded volume (random flight chain model) is reached, i.e., with the scaling like N^1. Below the Θ temperature the size of the chain starts to diminish rapidly. Eventually, at lower temperatures it forms a dense packed globule where the scaling of size parameters is like $N^{2/3}$. This behavior is qualitatively the same for linear chains as well as for branched ones. It has been shown that the only differences are in values of scaling exponents and temperatures of coil-to-globule transitions.[3−6]

In the case of stiff chains, the changes of their size with temperature are different from those for flexible ones. For moderate stiffness, the transition is rather smooth, and the low-temperature state is a dense packed globule without any local ordering. When the contribution of local energy (stiffness) becomes 2−3 times larger than that of long-range attraction, the transition becomes very sharp. For very stiff chains the transition becomes almost discontinuous. The low-temperature structure is formed by long sequences of extended conformations resembling secondary structures in globular proteins.[7−9] The recent Monte Carlo simulations of more complicated models of heteropolymers built on a (310) lattice lead to partially similar conclusions as the transition was not so sharp and the number of extended conformations in a collapsed state was much higher than that in the absence of a local potential.[10−12]

All the above-mentioned polymer chain models were simulated using a classical Metropolis sampling algorithm (MS), where a model chain underwent a simulated annealing.[13] This method has difficulties in sampling effectively the entire conformational space and is usually very inefficient at low temperatures. Recently a new version of the Metropolis algorithm called replica exchange (RE) has been invented.[14−16] In the replica exchange Monte Carlo, a set of replicas of a chain, is simulated simultaneously, each of them at a different temperature. The major difference between RE technique and an annealing sequence of simulations used in the MS scheme is based on the exchanges of conformations between replicas. This exchange transfers the system into a different part of the conformational space and thus helps chain to surpass local minima on the energy surface. The RE method was proved to be very efficient and useful for models with a similar level of simplicity, and thus it was selected to study the coil−globule transition in simplified lattice models of star-branched polymers.

It has also been shown that this new algorithm is very efficient in sampling the energy landscape while looking for the lowest energy conformation in simple polymer models.[17] It can also be pointed out that this algorithm is much faster giving similar description of coil-to-globule transition. The new algorithm combined with the histogram analysis allows one to study thermodynamics of the model system because it is capable—contrary to other Monte Carlo methods like the entropy sampling method— of converging in finite computational time for moderately long chains.[18]

In this paper, we have concentrated on the evaluation of the RE method applied to a simple models of branched polymer chains. We have chosen star-branched chains as a subject of this study because of their practical importance and their simplicity as a theoretical model of branched polymers. As the properties of the same model of star-branched and linear chains were determined in detail in other simulation studies using

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the classical Metropolis scheme, the evaluation of both new and old simulation methods can be easily done.[5,19]

The Model and the Algorithm

The model of polymer chain used in this paper was previously described in detail, and thus we give only a short outline here.[19,20] The chains were built on a simple cubic lattice. The chain had its own volume; i.e., it cannot cross itself. The contact attractive potential was introduced into the model in order to accommodate the influence of the solvent quality. The reciprocal of the attractive potential ϵ_a can be treated, as usual, as a temperature scale: $T^* = 1/\xi = kT/\epsilon_a$. The flexibility of chains was introduced into the model as a preference of some local conformations: extended conformations were energetically preferred. The parameter, which describes the stiffness, is depended on conformations of 3 consecutive chain segments. We defined the vector $\boldsymbol{r}_{14} = \boldsymbol{r}_{i+3} - \boldsymbol{r}_i$, where $\boldsymbol{r}_{i+3}$ and $\boldsymbol{r}_i$ are the positions of $(i + 3)$th and ith chain's bead respectively.[9] For $|\mathbf{r}_{14}| > 3$, local potential $\epsilon_{\mathrm{loc}} = 0$ while for $|\mathbf{r}_{14}| \leq 3$, ϵ_{loc} took a positive value. The values of ϵ_{loc} were varied in order to cover the case of partially flexible and stiff chain.

We used the two Monte Carlo algorithms. The first one was based on a classical Metropolis scheme frequently used previously for the same and similar polymer models.[19,20] The second one (replica exchange) was a modification of the first one. In both algorithms, the set of local micromodifications was applied for the efficient sampling of the conformational space. This set consisted of 2-bond motion, 3-bond motion, 3-bond crankshaft motion, end of chain reorientations, and collective motions of the branching point.[19,20] An attempt of a local motion was accepted due to geometrical constraints and excluded volume with a probability proportional to the Boltzmann factor for a given chain conformation.[20]

The first algorithm was based on the classical Metropolis scheme. The model chain was simulated at a given temperature. Then, the temperature was slightly lowered, the system was equilibrated, and the production Monte Carlo run was carried out. This annealing Monte Carlo sequence of simulations was repeated until approaching the temperature at which the model chain formed a dense packed globule. Many (over 20) independent simulation runs were made in order to obtain stable parameters describing the polymer chain.

The second algorithm was an extension of the first one. A set of M separate replicas of a given chain was simulated simultaneously. Every replica was simulated at a different temperature. The range of temperatures was chosen to cover the entire range: from the random coil state to the dense globule state. The temperature distances between replicas were similar to temperature changes in the Metropolis annealing algorithm. Every replica was simulated using the described above Metropolis Monte Carlo algorithm. After some Monte Carlo steps the attempt of the exchange between a pair of replicas took place. The temperature range was chosen in order to cover the expanded chain (random coil conditions) and the collapsed globule: T was between 0.5 and 5. Simulation of every temperature point (every replica) consisted of 10^7 time units and was preceded by the 10^6 time units of equilibration run. Each pair of neighboring replicas was attempted to exchange every 10^3 time units. Having two replicas, ith simulated at the temperature T_i and jth at the temperature T_j, one can define the following exchange probability

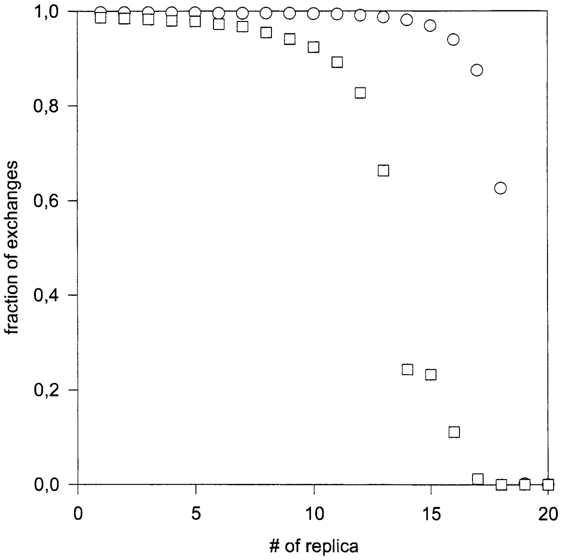

Figure 1. Fraction of successful exchanges of replicas vs the number of replicas. The case of the stiff (st = 4) star-branched chain consisted of $N = 49$ (open circles) and $N = 200$ segments (open squares).

$$p_{ij} = \begin{cases} 1 & \text{for} \quad \Delta \leq 0 \\ \exp(-\Delta) & \text{for} \quad \Delta > 0 \end{cases}$$

with

$$\Delta = \left(\frac{1}{k_B T_i} - \frac{1}{k_B T_j}\right)(E_j - E_i)$$

where k_B is the Boltzmann's constant; E_i and E_j are energies of ith and jth replica, respectively. Because of the first contribution to the Δ factor, the exchanges of replicas that came from quite different temperatures is rather unlikely. Because of that we limited our algorithm to exchanges between the pairs of replicas which were at neighboring temperatures. Recently, it has been shown that different distributions of temperatures of replicas does not affect the results,[17] and therefore, we have chosen a linear set of temperatures. The parameters that influenced the stability and the convergence of the calculated parameters will be discussed below.

Results

Simulations were carried out for models of star-branched chains consisting of $f = 3$ arms of equal length. The total chain length was changed in order to determine its influence on the location and properties of the coil–globule transition in both simulation methods. The total number of polymer segments N was varied as usual between 49 and 799. Calculations were carried out for the stiffness parameter st $= \epsilon_{\mathrm{loc}}/\epsilon_a$ taking the following values: 0 (fully flexible chain), 2, 4, and 8. The results presented below concern the series of 25 independent simulation runs for every set of parameters N, ϵ_a, and ϵ_{loc} and for both methods. In the RE method, $M = 20$ replicas were simulated simultaneously, and the temperature was in the same range as previously in MS simulations of this model.[20] The difference in temperature between adjacent pairs of replicas was between 0.02 and 0.03.

Figure 1 presents the fraction of successful exchanges between the replicas as a function of the replica's

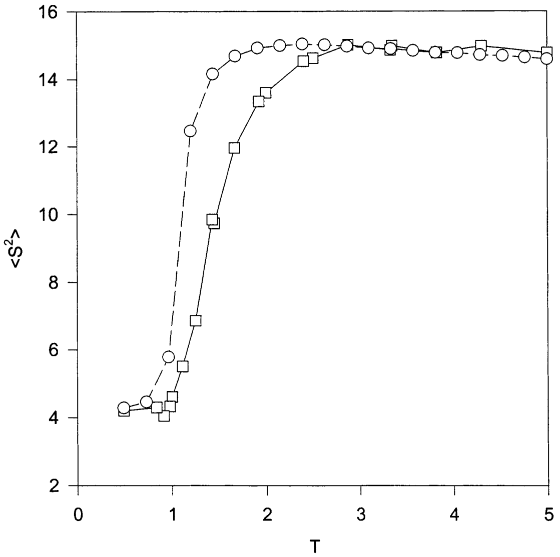

Figure 2. Mean-square radius of gyration $\langle S^2 \rangle$ vs the temperature T for the stiff star-branched chain consisting of $N = 49$ segments (st = 4): the MS algorithm (open squares) and the RE algorithm (open circles).

number (the number of a replica increases with the decreasing of the temperature) for two different chain lengths. One can observe that for all cases at high temperatures this fraction is just below 100%. Going down with the temperature, a steep decrease of these fractions took place and for the lowest temperatures it is on the level of 1%. The last replica (at the lowest temperature) shown at Figure 1 can be rejected from the simulation procedure, as it simply does not exchange any replicas. The increase of the chain length shifts the point where the fraction of the replica exchange decreases rapidly toward the higher temperatures. The region of the rapid decrease of the exchange rate is apparently located near the coil−globule transition temperature (see below). This type of changes in the exchange rate confirms that the algorithm used is the proper one and that in the most important region; i.e., near coil−globule transition the fractions of successful exchanges are high enough to introduce new conformations and thus to avoid trapping the chain in deep local minima of energy.

The next series of figures presents the comparison of commonly used parameters that describe the properties of the model chain at various temperatures, i.e., the mean-square radius of gyration of the entire star-branched macromolecule, the mean total energy of the system and the heat capacity (calculated as the dispersion of the energy) obtained in both simulation methods.

In Figures 2−4, one can observe the changes of the mean-square radius of gyration of the entire star macromolecule $\langle S^2 \rangle$ with the temperature T for chains of different lengths and stiffness. In both simulation methods, this parameter decreases with the decreasing of the temperature from values characteristic for random coil to those of a dense packed globule.[19−22] At high temperatures, MS and RE methods give us almost the same size of the chain (the differences are on the level of standard error). But in the coil-to-globule transition region one can observe that the values of $\langle S^2 \rangle$ differ significantly. The changes of the radius of gyration are more rapid for the RE method. Moreover, the changes of $\langle S^2 \rangle$ for this method are located at lower temperatures. This implies that the temperatures of the coil-to-globule transitions determined in the MS method are probably too high. The differences between these two simulation methods very weakly depend on the chain length—values of the radius of gyration near the transition differ for ca. 20% for short chains ($M = 49$, st = 0) and for ca. 25% for long chains ($n = 799$, st = 0). The introduction of stiffness into the model has a weak influence on these differences too—differences between the two methods are higher for higher values of the parameter st.

The differences between the mean energies of the chain, which were calculated using both simulation methods under consideration, are presented in Figures 5−7. One can observe that these differences are considerably smaller while compared to the size parameter, i.e., radius of gyration, discussed above. There are no big differences in the high-temperature regions. At the low temperatures where the dense packed globule is

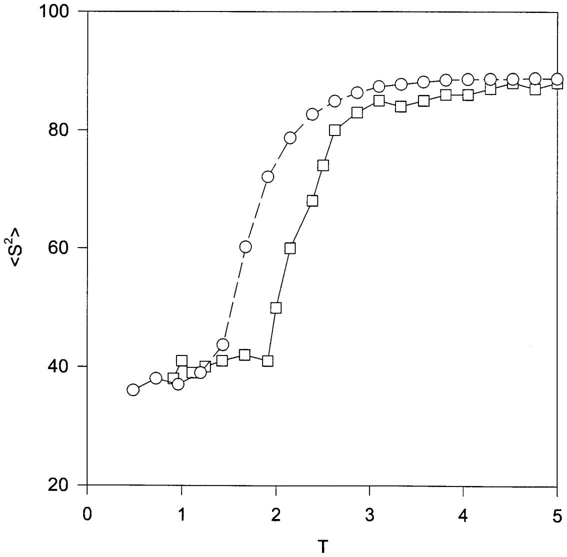

Figure 3. Mean-square radius of gyration $\langle S^2 \rangle$ vs the temperature T for the stiff star-branched chain consisting of $N = 199$ segments (st = 8): the MS algorithm (open squares) and the RE algorithm (open circles).

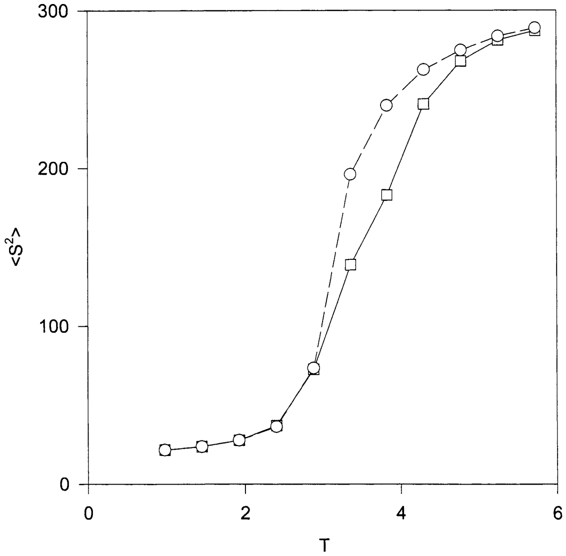

Figure 4. Mean-square radius of gyration $\langle S^2 \rangle$ vs the temperature T for the flexibble star-branched chain consisting of $N = 799$ segments (st = 0): the MS algorithm (open squares) and the RE algorithm (open circles).

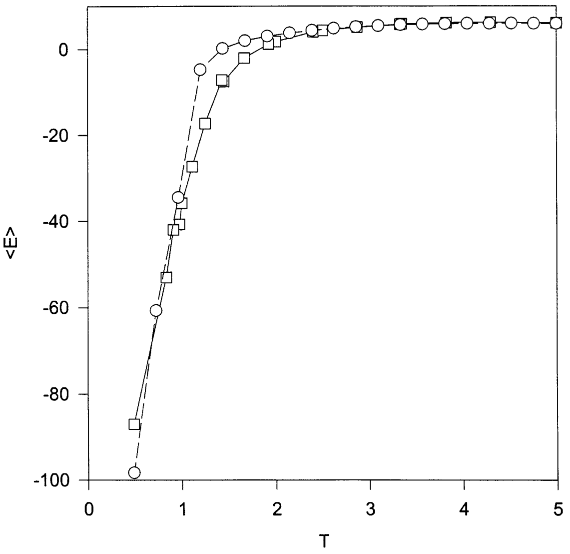

Figure 5. Mean energy $\langle E\rangle$ vs the temperature T for the stiff star-branched chain consisting of $N = 49$ segments (st = 4): the MS algorithm (open squares) and the RE algorithm (open circles).

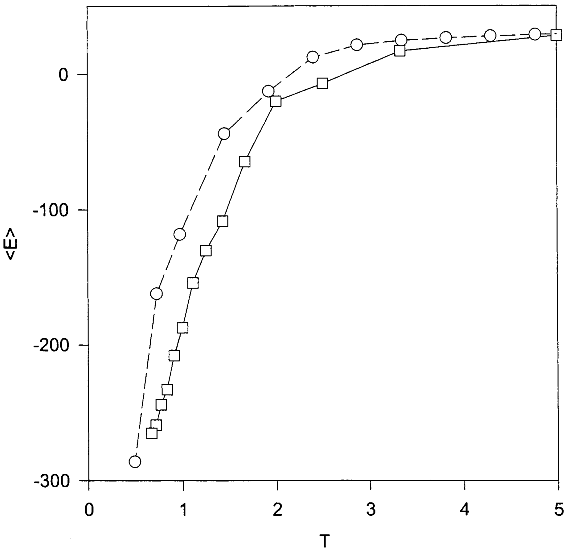

Figure 6. Mean energy $\langle E\rangle$ vs the temperature T for the stiff star-branched chain consisting of $N = 199$ segments (st = 8): the MS algorithm (open squares) and the RE algorithm (open circles).

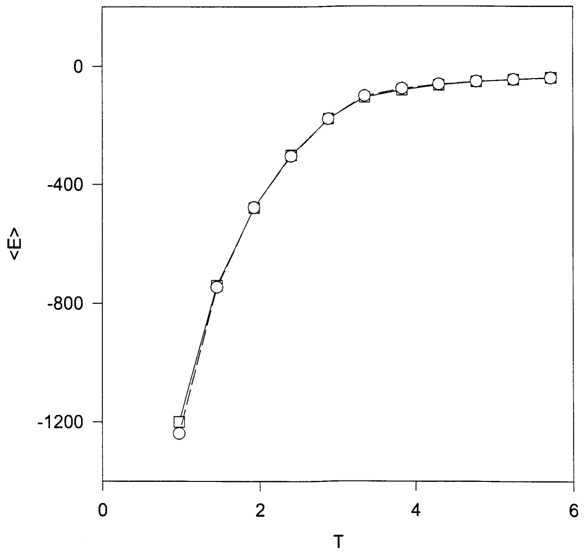

Figure 7. Mean energy $\langle E\rangle$ vs the temperature T for the flexible star-branched chain consisting of $N = 799$ segments (st = 0): the MS algorithm (open squares) and the RE algorithm (open circles).

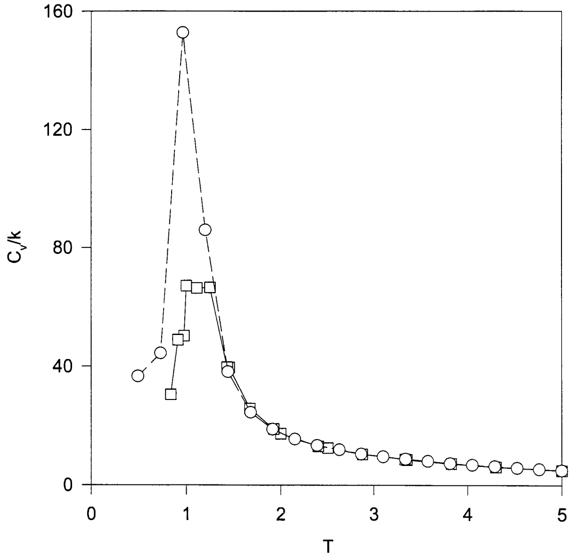

Figure 8. Heat capacity $\langle C_V/k\rangle$ vs the temperature T for the stiff star-branched chain consisting of $N = 49$ segments (st = 4): the MS algorithm (open squares) and the RE algorithm (open circles).

expected to be formed the results for both methods differ. In the vicinity of the transition region, the energy calculated by the Metropolis method is in general 10% smaller than that calculated by the RE method. In other words, the RE curve is slightly steeper in the transition region. The increase of these discrepancies rises weakly with the increase of the chain length and with the stiffness parameter st. One can observe that in the case of the chain with $N = 199$ beads and stiffness st = 8, the differences between energies calculated by these both methods are significant in the entire temperature range, i.e., $0.5 < T < 5$. However, for the case of a very stiff chain, the energies calculated according to MS method were lower than those obtained by the RE method. Only for the lowest temperatures does it seem that RE results would be below those of the MS method (it is impossible to carry out simulations at lower temperatures as the sampling algorithm are completely inefficient). Similar behavior was found for all chain lengths under consideration with st = 8. It is difficult to explain this behavior of the energy, but it probably was caused by the fact that for this stiffness the transition was located at very low temperatures and the fully collapsed globule was actually out of our reach.

Figures 8–10 present the changes of the heat capacity with the temperature. One can observe that in general the position of the first peak (going from high to low temperatures) is very close in both simulation methods. This means that the coil-to-globule transition temperatures estimated in the MS method as a position of the heat capacity peak are rather correct although for the RE method the transition temperatures were found to be lower. One can also observe that the heat capacity curves are smoother in the RE method, and contrary to the MS algorithm where there is no second peak at the lowest temperatures. The existence and explanation of that second peak was not clear, although it was suggested that some kind of rearrangement of the chain

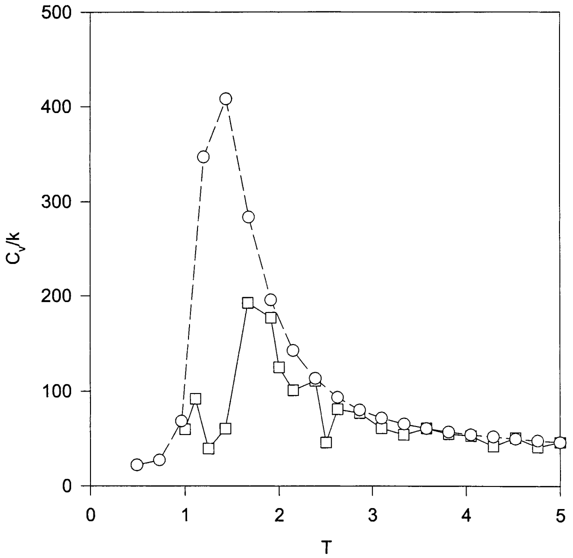

Figure 9. Heat capacity $\langle C_V/k \rangle$ vs the temperature T for the stiff star-branched chain consisting of $N = 199$ segments (st = 8): the MS algorithm (open squares) and the RE algorithm (open circles).

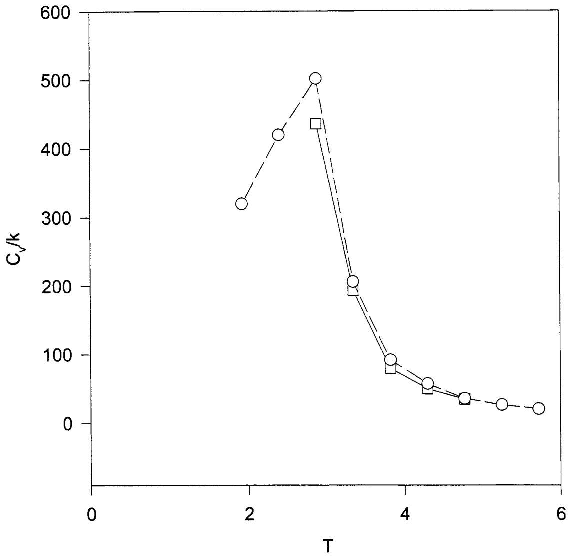

Figure 10. Heat capacity $\langle C_V/k \rangle$ vs the temperature T for the flexible star-branched chain consisting of $N = 799$ segments (st = 0): the MS algorithm (open squares) and the RE algorithm (open circles).

takes place below the coil-to-globule transition.[10,12] The appearance of more than one peak on C_v curves was also reported for homopolymers studied by the means of discontinuous molecular dynamics and Monte Carlo simulations.[23] This was explained by the presence of gas-to-liquid, liquid-to-solid, and solid-to-solid transitions. Similar behavior was observed for flexible Lennard-Jones chains.[24] The strong local potential prefers extended conformations (in the 310 lattice model these conformations correspond to α-helices and β-strands). The collapse of the chain is a competitive process to the forming of extended conformations. Thus, it was thought that the attractive potential prevails at first when the collapsed structure appears. Then, the local potential starts to play the main role, and longer helices are formed, partially destroying the compactness of the globule. Now, we can argue that it was caused by the weak statistics only, as the MS algorithm was rather inefficient for low temperatures and the system visited a very limited part of the conformational space. We have also used the exponential set of temperatures where more replicas were at lower temperatures. The introduction of this set of produced nearly the same results as by the linear one. Even in the case of the heat capacity, the results were very close. On the other hand, the statistical error obtained in the exponential set is slightly larger while comparing that set to the linear ones. Kolinski et al. have reported a similar case.[18]

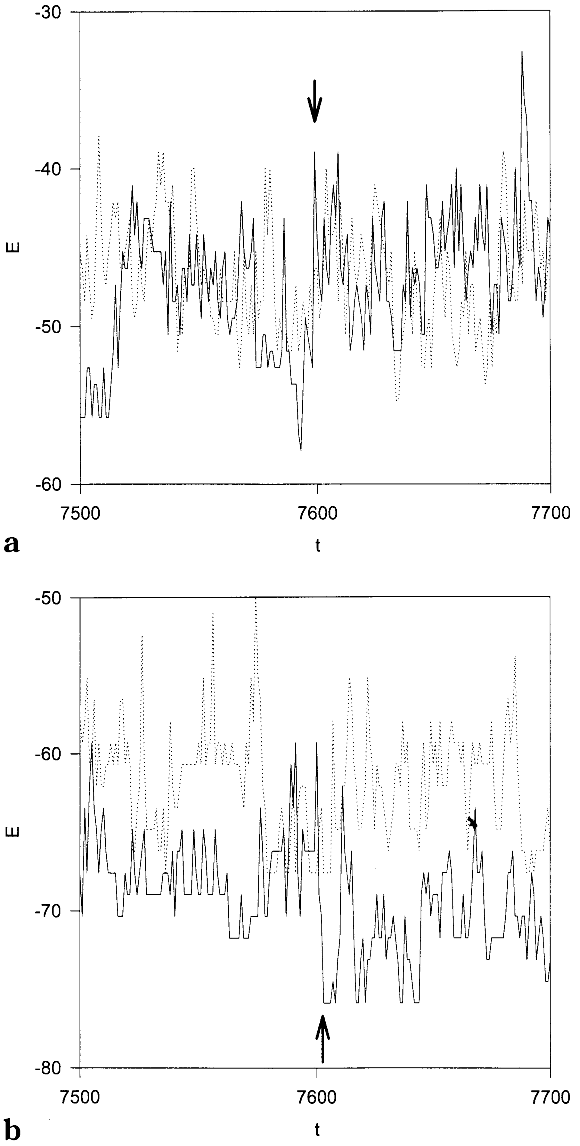

Figure 11. Energy E vs the time t for the flexible star-branched chain consisting of $N = 49$ segments: the MS algorithm (dotted lines) and the RE algorithm (solid lines), both at temperature $T = 0.94$ (a) and 0.73 (b). The arrows indicates the time $t = 7600$ where the exchange of both replicas took place.

Figure 11 presents an example of the energy flowcharts of the MS simulation run and that of the RE simulation at both lowest temperatures under consideration. In both cases, the temperatures ($T = 0.95$ and 0.73) and all other parameters ($N = 49$, st = 0) were exactly the same. One can observe that in the case of higher temperature, $T = 0.95$, the differences between the energies reached by the model system are smaller than for the lowest temperature, $T = 0.73$. At the lowest temperature the differences between results obtained by the two methods are more pronounced. The range of

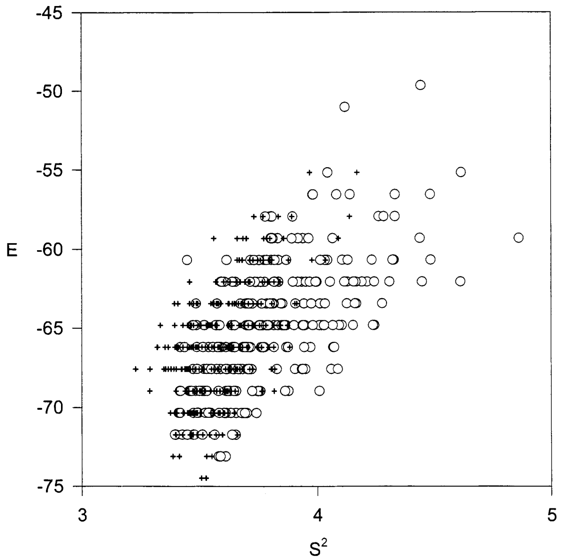

Figure 12. Energy of the chain E vs the squared radius of gyration S^2 for the case of the flexible chain (st = 0) with $N = 49$ segments at temperature $T = 0.73$ for the MS algorithm (open circles) and the RE algorithm (crosshairs).

the energy fluctuations is comparable at both temperatures. The process of the exchanges of model chains between these two replicas can be observed. for time $t = 7600$. This exchange was unlucky for replica no. 19 ($T = 0.95$) where the energy become considerably higher and lucky for replica no. 20 ($T = 0.73$) where the energy become even more considerably lower. The change of the chain conformation helped further search for the low energy state: the energy of replica no. 20 went down for some time units after the exchange. On the other hand, replica no. 19 recovered within the same time; i.e., its energy came back to its value before the exchange.

The next question we wanted to answer in this paper was the problem of finding the lowest energy state of the system. From the computational point of view, the time spent by the chain looking for the low energy states also differs both methods: in the RE method, it is considerably faster. In Figure 12, we present the dependence of the chain's energy on the chain's size (squared radius of gyration) for the lowest temperature under consideration. Most conformations of the chain obtained by the RE simulation have lower energy and smaller size compared to those obtained by the MS method. One can observe that the lowest energies (regardless to the simulation method used) do not correspond to the smallest value of S^2. It implies that the low-temperature structures are not globules consisting of polymer segments only, but some solvent molecules are also present inside the collapsed chain.

The above findings are in a very good agreement with the recent results obtained in the simulations of other models of linear chains:[17]

(i) The coil−globule transition temperatures estimated in the MS method are too high. The differences are especially large for longer chains. It means that actually the classical Metropolis algorithm is applicable to good solvent conditions only and not capable for lower temperatures. The differences are higher for stiffer chains because the structure of a energy surface becomes more complicated comparing with flexible chains and the MS algorithm has even more difficulties in searching low-temperature structures.

(ii) The character of the coil−globule transition is similar for both methods only in the case of fully flexible (st = 0) and partially flexible (st = 2) chains. For stiff chains (st = 4 and 8) the transition is much steeper in the RE method. This effect is also visible for longer chains (see Figure 4—the case of $N = 799$). The transition is not cooperative because we deal with the homopolymer chain.

The major conclusion that can be drawn from the above studies is that most of the up to date Monte Carlo simulations of temperature-dependent properties of polymer chains were rather crude. The new replica exchange simulation technique enables one to study models of polymer chain at low temperatures and to estimate the real coil-to-globule transition temperature. The next step of these studies should contain the combination of the replica exchange and the histogram method which should give us a full thermodynamic description of the coil−globule transition.[18]

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