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Thermodynamic Properties of Star Shaped Polymers Investigated with Wang-Landau Monte Carlo Simulations

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Summary: Entropic sampling method within Wang-Landau algorithm is used for simulation of lattice models of linear polymer chains and 6-arm star-shaped polymers. The semi-phantom (i.e. nonreversal) random walk on 3D simple cubic lattice is used as a reference system. The densities of states are obtained and on their basis the temperature dependences of internal energy, heat capacity, entropy and mean square radius of gyration are calculated. Results for stars are compared with data for linear chains.

Keywords: Monte Carlo; polymers; star polymers; Wang-Landau algorithm

Introduction

Monte Carlo (MC) method is a powerful tool in studying a large variety of molecular systems. We apply an efficient version of Monte-Carlo method, the entropic sampling (ES) [1,2] within Wang-Landau (WL) algorithm,[3] to investigate lattice models of linear and star-like polymers starting with a single neutral polymer chain. The efficiency of ES-WL algorithm for simulations of polymer lattice models was demonstrated in previous works of our group [4–9] and of other authors.[10–14]

Complicated polymer systems such as stars, brushes or dendrimers attract much attention during last decades being subjects of a number of theoretical [15,16] and experimental [17,18] studies. It is important that star polymers can be used for DNA and drug delivery into living cells;[17,18] they are also applied for transport and separation of metal cations in a liquid membrane system.[19] Star polymers can be regarded as the simplest branched-type polymers where multiple linear chains are connected to a common core. So their investigation can serve as a key to understanding the properties of more complex polymer architectures such as dendrimers.[20]

Analytical treatment in theory of star polymers meets with great difficulties due to their fairly complex architecture hence their computer simulation becomes rather important.[21,9,10] In the present work we investigate thermodynamic and structural properties of star-lake polymers and compare them with properties of linear chains. Specifically interesting is to obtain thermal and structural properties (internal energy, heat capacity, entropy, mean square radius of gyration) as functions on temperature. It is helpful also to understand the transition phenomena in the investigated models.

The structure of the article is as follows. Section *Model and method* contains detailed description of the model used in our study and the algorithm of our program. In section *Results and discussion* we consider athermal and thermal cases and present results of our simulations for chains and stars. Section *Conclusion* contains final remarks.

Model and Method

In our simulations we use a semi-phantom (nonreversal [21]) random walk [5] on a simple cubic lattice with a unit step as a

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basic reference system. The term semi-phantom random walk implies that the back (reversal) steps are prohibited. The chain of length N has N bonds and $N+1$ monomers (lattice nodes). The polymer is described by a set of coordinates (x_i, y_i, z_i), where $i=[0,N]$. The first point and the first segment of the chain are fixed. The other segments are generated as a semi-phantom walk. The arms of the star polymer are generated in the same way.

In order to modify the conformation of the chain or the arm of the star we select randomly one of the nodes from 1 to N-l (monomer k_0) and change randomly and nonreversally the coordinates of the monomers between k_0 and k_0+l where l is the number of segments in the modified piece. The length of the modified piece is taken in the range $[N/20] \div [N/10]$. The rest of the chain (the tail $[k_0+l,\ N]$) undergoes a parallel shift, taking into account that after this shift the chain should remain semi-phantom (otherwise we rebuild the last segment of the modified piece).

We consider two cases: athermal and thermal. The athermal case signifies exclusion of intersections (overlaps of monomers) and taking into account only self-avoiding conformations (SACs) among generated semi-phantom chains. The ratio of SACs yields excess entropy. In the thermal case interactions of nonbonded monomers in a SAC are accounted for. We attribute the energy ε ($\varepsilon>0$ or $\varepsilon<0$) to each nonbonded monomer pair occurring at a unit distance (closest contact). So the potential between two nonbonded monomers is given by:

$$u(r)=\begin{cases}\infty & r=0\\ \varepsilon & r=1\\ 0 & r>1\end{cases} \tag{1}$$

The SACs are selected homogeneously from the generated semi-phantom trajectories.

In the thermal case we obtain the distribution as a function of the number of contacts m that is equivalent to the distribution as a function of the energy, since in our model the energy of the polymer is $E_m=\varepsilon m$. This distribution is obtained within WL procedure [3] in the following way. The range of contacts $[0,m_{\max}]$ is divided into $N_b=m_{\max}+1$ elements ("boxes") so that i-th box corresponds to conformations having i contacts. We do not have an exact expression for $m_{\max}$, but for the chains there exists an estimate [22]

$$\begin{aligned} m_{\max} &\le \mathrm{Int}[a_c N - d(N+1)^{\Delta b} + d] \\ &= \mathrm{Int}[2N - 3(N+1)^{2/3} + 3], \end{aligned} \tag{2}$$

where N is the chain length; $d=3$, space dimension; $a_c=d-1$, $\Delta b=(d-1)/d$. For stars $m_{\max}$ is slightly lower than for chains because of the imposed restrictions — grafting of arms to the common center. The array $\tilde{g}$ including N_b elements is introduced, each of them corresponding to its own energy. Initially all elements of $\tilde{g}$ are taken equal to unity. It appears to be more convenient to use the array of quantities $\tilde{S}(E)=\ln\tilde{g}(E)$ (initially all $\tilde{S}_i=0$). At each MC step the conformation of the system is modified in the manner described above. Let $E_i=m_i\varepsilon$ and $E_j=m_j\varepsilon$ be the energies of the system before and after modification. Each of them hits its own box — i or j respectively (i and j can coincide). In this case the transition is accepted with the probability [3]

$$\begin{aligned} p(E_i\to E_j) &= \min\left(1,\frac{\tilde{g}_i}{\tilde{g}_j}\right) \\ &= \min\left(1,e^{\tilde{S}_i-\tilde{S}_j}\right), \end{aligned} \tag{3}$$

where $\tilde{g}_i$, $\tilde{g}_j$, $\tilde{S}_i$, $\tilde{S}_j$ are **current** values of i-th and j-th elements of the array $\tilde{g}$ and $\tilde{S}$ correspondingly (actually we operate only with the array $\tilde{S}$). In the case of failure the system remains in the initial state. At each visit of k-box (in case of acceptance new conformation $k=j$, in case of nonacceptance $k=i$) we change the k-th element of $\tilde{S}$: $\Delta\tilde{S}$ is added to $\tilde{S}_k$. A number of these steps constitute a sweep during which $\Delta\tilde{S}$ is kept constant. At each next sweep $\Delta\tilde{S}$ is reduced: $\Delta\tilde{S}\to c\Delta\tilde{S}$ with increment $0<c<1$. We used $c=0.8\div0.9$ and the initial value

$\Delta\tilde{S} = 0.001$. The number of sweeps used was in the range $30 \div 60$.

Simultaneously with the array $\tilde{S}$ the array of visits $\boldsymbol{V}$ with zero initial values is introduced. At each MC step we add 1 to V_k-element that corresponds to a visit of the state k. We watch that during calculations the histogram of visits becomes and holds further sufficiently uniform (“flat”). Using this way ES-WL algorithm the auto adjustment of visit probabilities is achieved.

At the end of the computer experiment when the array of visits becomes homogeneous the array of density of states is calculated as $\exp(\tilde{S}(E))$ and is normalized to unity (we designate it as $g(E)$). This normalization is important for calculating the canonical part of entropy and free energy.

Results and Discussion

Test of the Method (Polymer Chains)

The main aim of our work is the investigation of star shaped polymers. We precede it by testing the method on linear chains.

In the first test the distribution of semi-phantom random walks as a function of the number of intersections n for chains of several lengths was estimated (Figure 1). This distribution is obtained with the aid of ES-WL-procedure in the same way as it is described before. In this case the range of n $[0, n_{\max}]$ is known exactly. The expression for $n_{\max}$ is given below (see equation 4). The range of n is divided into elements (boxes) so that the i-th element corresponds to conformations having i intersections. Accordingly, we have $N_b = n_{\max} + 1$.

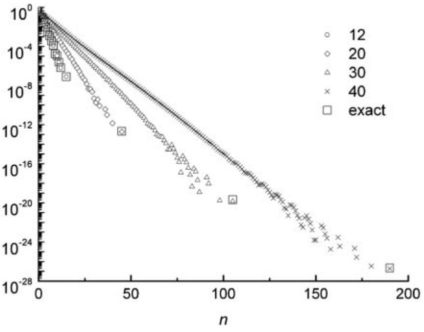

Figure 1.

Distribution of the number of semi-phantom conformations as a function of the number of intersections for $N = 12$ (circles), 20 (diamonds), 30 (triangles), 40 (crosses) [9]. Squares indicate the exact data.

The results of the test (Figure 1) are in good agreement with the available exact data. For small N (e.g. for $N = 12$) all values of n can be calculated by direct enumeration of all $6 \cdot 5^{N\text{-}1}$ semi-phantom conformations. For greater n it becomes difficult though for arbitrary N the exact data can be obtained for the maximum number of intersections for which the probabilities are the smallest.

Indeed the maximum number of intersections for a semi-phantom chain with the length N corresponds to a square with a unit side length and it can be determined by an exact formula:

$$n_{\max} = 3C^2_{\left[\frac{N}{4}\right]} + C^2_{\left[\frac{N}{4}\right]+1} + x\left[\frac{N}{4}\right], \qquad (4)$$

where [] is the integer part of the argument, $C^2_{[N/4]}$ and $C^2_{[N/4]+1}$ are the binomial coefficients, $x = N - 4\left[\frac{N}{4}\right]$ and can have values $x = 0, 1, 2, 3$. Proof of (3) is presented in Appendix 1.

It is very important that the number of such conformations (number of squares) does not depend on N and is equal to $6 \cdot 4 = 24$ (6 directions with 4 cases for each direction). So the corresponding normalized value of g relatively to the total number of conformations for the semi-phantom chain, $6 \cdot 5^{N\text{-}1}$, is $g_{n_{\max}} = 4 \cdot 5^{1-N}$

Figure 1 shows that our algorithm enables us to safely obtain distributions with probability at least down to $10^{-27.}$ For $N = 12$, 20, 40 exact values are $g_{n\max} = 8.19 \cdot 10^{-8}$, $2.10 \cdot 10^{-13}$, $2.20 \cdot 10^{-27}$, against the obtained ES-WL values $g_{n\max} = 8.07 \cdot 10^{-8}$, $1.90 \cdot 10^{-13}$, $1.94 \cdot 10^{-27}$. So the deviations of calculated values from the exact ones in points of the smallest probabilities are within 10%.

As a result of the second test the distributions of SACs g_{0m} as a function of the number of contacts for $N = 12$, 30, 50,

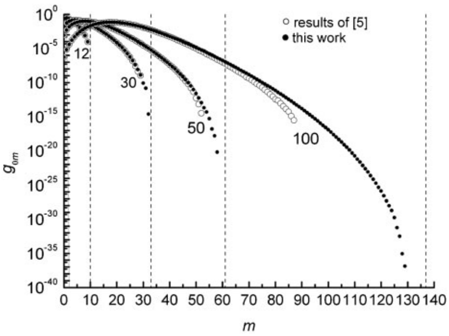

Figure 2.
Distribution of self-avoiding conformations (SACs) as a function of the number of contacts for $N = 12$, 30, 50, 100 (points – this work) [9]. Open circles – data from work [5] (based on phantom random walks) Vertical dashed lines are the estimation of $m_{\max}$ for chains [22]. Subscript "0" in g_{0m} denote that we consider conformations with 0 intersections.

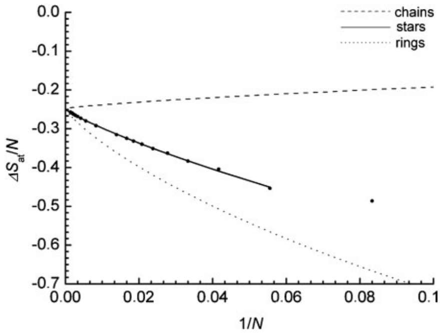

Figure 3.
Specific excess entropy (relatively to the entropy of a phantom chain) as a function of inverse number of segments for stars (filled dots) – WL data, approximated by least-squares fit (solid line) of the function $f(x) = Ax\ \ln(x) + Bx + D$; $x = 1/N$ [9]. For comparison results for chains (dashed line) and for rings [5] (dotted line) are presented.

100 are presented in Figure 2 in comparison with data from.[5] Subscript "0" in g_{0m} denotes that we consider conformations with 0 intersections, subscript "m" denotes the number of contacts. Vertical dashed lines in Figure 2 are the estimation of $m_{\max}$ for chains[22] (equation 2). There is a good agreement of our data with that from[5] in a wide range of m though at largest m a discrepancy is observed. For the greatest N ($N = 100$) the discrepancy at large m is the greatest. Here the advantage of semi-phantom random walk in comparison with the phantom one is clearly demonstrated: it enables us to obtain the distribution in a much wider range of contacts than on the basis of phantom ones[5] (Figure 2). There still remains a problem of modeling the compact conformations which make an essential contribution to the energy at low temperatures in the case of attraction.[9]

Star Polymer

The model of a 6-arm star polymer is considered and the excluded volume effect in the athermal case is studied first. The specific excess entropy (relative to the entropy of a corresponding phantom chain) as a function of the number of monomers N in the star polymer is obtained and its dependence on the inverse number of segments for stars is presented in Figure 3 compared with analogous data for chains and for rings.[5] The WL data is approximated by a least-squares fit (solid line) of the function $f(x) = Ax\ln(x) + Bx + D$; $x = 1/N$ in much the same way as it was done in work.[5] The character of this function corresponds to the logarithm of the well-known scaling asymptotic relation for linear chains.[4] The coefficients obtained for stars: $A = 0.7399$, $B = -1.4837$, $D = -0.2494$, (in the case of rings they are: $A = 1.6996$, $B = -0.7795$, $D = -0.2495$;[5] for chains from the scaling relation: $A = -0.1667$, $B = 0.1570$, $D = -0.2476$). It is seen from Figure 3 that at $N \to \infty$ the specific excess entropy for all three systems, stars, rings and chains, tends to the common limit: values of coefficients D are very close to each other.

In the thermal case we compare polymer chains and stars with the same number of segments ($N = 30$, 72, 120). The distributions g_{0m} as a function of the number of contacts (energy) for free chains and stars obtained with the aid of WL-algorithm are presented in Figure 4. The comparison shows that difference between distributions for chains and stars is noticeable though not

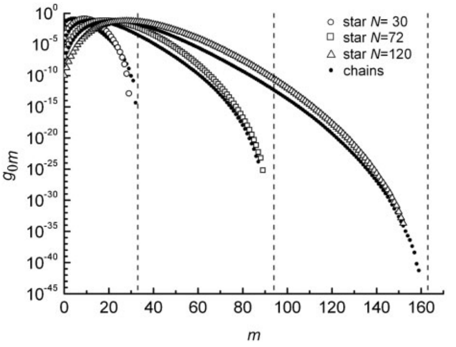

Figure 4.
Normalized distributions for SACs as a function of the number of contacts for star with $N = 30$ (circles), 72 (squares), 120 (triangles) and for the chains with equal number of segment (dots) [9]. Vertical dashed lines are the estimation of $m_{\max}$ for chains [22].

drastic. The maxima of distributions for stars ($m = 9, 18, 28$) are shifted to greater m relatively to those for chains ($m = 4, 12, 22$). The reason is that segments in a star are closer to each other than in a chain because stars' arms are fixed at their center. With the increase of N the relative differences in positions of these maxima become smaller.

Distributions g_{0m} enable us to obtain the thermodynamic properties of investigated systems such as internal energy, free energy, entropy and heat capacity in a wide temperature range.

Using g_{0m} we calculate the thermodynamic properties:

1) Internal energy:

$$\langle E\rangle(T) = \frac{\sum\limits_{m=0}^{m_{\max}} E_m \exp(-\beta E_m) g_{0m}}{\sum\limits_{m=0}^{m_{\max}} \exp(-\beta E_m) g_{0m}},$$

$$E_m = \varepsilon m \tag{5}$$

2) Heat capacity:

$$C = \frac{\partial\langle E\rangle(T)}{\partial T} \tag{6}$$

It is equivalent to the fluctuation equation $C(T) = (\langle E^2\rangle(T) - (\langle E\rangle(T))^2)/T^2$.

3) Entropy:

$$S(\beta) = S_0 + \Delta S_{\mathrm{at}} + \Delta S(\beta) \tag{7}$$

$$S_0 = N \ln \nu \tag{8}$$

$$\Delta S_{\mathrm{at}} = (N-1)\ln\frac{\nu-1}{\nu} + \ln\frac{(\nu-2)!}{(\nu-1)^4} + \ln g_0 \tag{9}$$

$$\Delta S(\beta) = \beta\langle E\rangle + \ln\sum_{m=0}^{m_{\max}} e^{-\beta\varepsilon m} g_{0m}, \tag{10}$$

where S_0 — entropy of the phantom chain, ν — the number of nearest neighbors for the lattice, ΔS_{at} — excess athermal part of the entropy for the star (see Figure 3), proof of (9) is presented in Appendix 2, $\Delta S(\beta)$ — thermal (canonical) part of the entropy, $\beta = 1/k_B T$ is the inverse temperature. In Figures 5–8 temperature is presented in energy units, i.e. designation $T' = k_B T/|\varepsilon|$ and inverse temperature $\beta' = 1/T'$.

In Figures 5–7 the dependences of specific energy, specific heat capacity, and specific excess entropy on temperature are presented in the repulsion case ($\varepsilon > 0$). It is seen that for linear chains of different length the dependences of specific energy on temperature (Figure 5) rises with the increase of N but differ not strongly from each other with a tendency to a certain limiting curve. For stars with the same number of segments the difference is

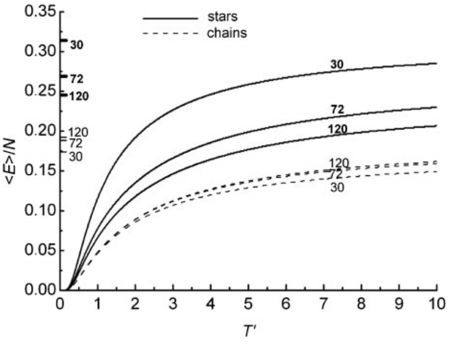

Figure 5.
Dependences of specific energy on temperature for stars (solid lines) and chains (dashed lines) [9], $\varepsilon > 0$. $\langle E\rangle/N$ is in $|\varepsilon|$ units. At the Y-axis the limiting values of $\langle E\rangle/N$ for $T \to \infty$ are labeled. At $T \to 0$ $\langle E\rangle/N \to 0$.

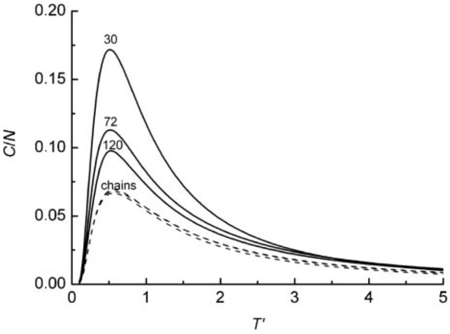

Figure 6.
Dependences of specific heat capacity on temperature for stars (solid lines) and chains (dashed lines); $\varepsilon > 0$ [9].

appreciably greater and with the increase of N the level of curves falls. Energy for a star is greater than for a chain with the same number of segments. At $T = 0$ we have $\langle E\rangle/N = 0$, and at $T \to \infty$ we get $\langle E\rangle/N \to \varepsilon\langle m\rangle_{\mathrm{at}}(N)/N$, $\langle m\rangle_{\mathrm{at}} = \sum_{m=0}^{m_{\max}} m\, g_{0m}$ [4]. Limiting values of $\langle E\rangle/N$ at $T \to \infty$ for the star decreases with the increase of the number of segments, while for chains they increase. So we can suppose, than for $N \to \infty$ the $E/N(T)$ dependences for stars and chains tend to the same limiting curve.

Each T-dependence of the specific heat capacity (Figure 6) has a single maximum both for chains and stars, at about $T = 0.52$ that signifies structure changes in the molecules. It should be pointed out here that in the case of attraction the increase of the chain length results in sharpening in the temperature dependencies of the heat capacity that corresponds to change of structure having features of the phase transition. Such behavior was observed in[10,14] in simulations of non-charged polymer systems and in modeling of polyelectrolytes.[7] In the case of repulsion presented in this work there is observed a smooth transition from purely athermal case (SACs) for high temperatures to complete avoidance of contacts at low temperatures. The latter can be regarded as an effective "swelling" of polymer chains or star arms.

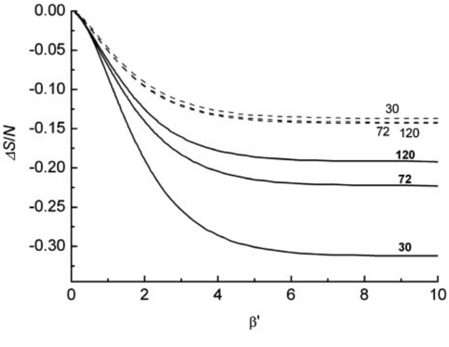

Figure 7.
Dependences of specific excess entropy on inverse temperature for stars (solid lines) and chains (dashed lines); $\varepsilon > 0$ [9].

Behavior of entropy (Figure 7) has the same features as that of energy and heat capacity. Entropies fall with the decrease of temperature, for stars the curves are lower than for chains and there is a tendency to reach some common limiting curve with the increase of N.

The above results are presented for the case of repulsion between monomers. Corresponding dependences in the case of attraction ($\varepsilon < 0$) are more complex and are presented with other corresponding data in.[9]

Using distribution g_{0m} (Figure 4) we can also express the mean square radius of gyration dependence on temperature $\langle R^2\rangle(T)$ using the relation

$$< R^2 > (T) =<< R^2 >_m> (T) = \frac{\sum_{m=0}^{m_{\max}} < R^2 >_m \exp(-E_m\beta) g_{0m}}{\sum_{m=0}^{m_{\max}} \exp(-E_m\beta) g_{0m}}, \qquad (11)$$

where $\langle R^2\rangle_m$ is the average of square radius of gyration obtained for each number of contacts m during calculations of g_{0m}.

Dependences of $\langle R^2\rangle(T)$ for chains and stars are presented both for $\varepsilon < 0$ and $\varepsilon > 0$ in Figure 8a,b.

Mean square radius of gyration determines the size of the molecule. For $\varepsilon > 0$ dependences monotonically decrease and for $\varepsilon < 0$ they monotonically increase with temperature. At $T \to \infty$ the dependences for $\varepsilon > 0$ and $\varepsilon < 0$ tend to a common limit. For

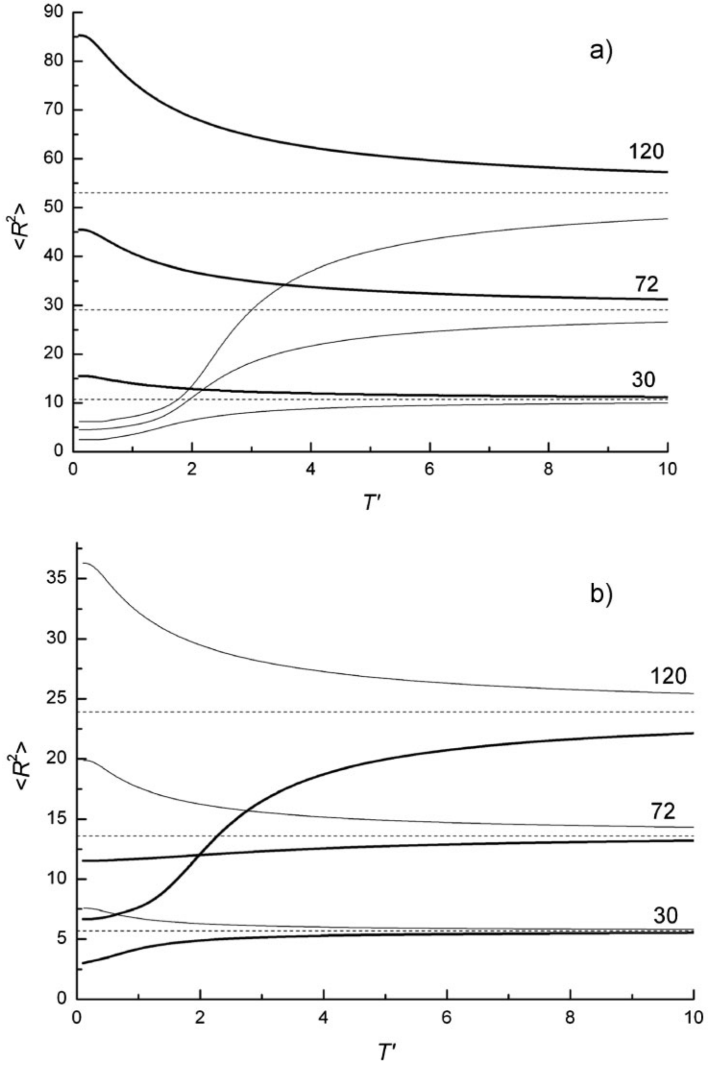

Figure 8.

Mean square radius of gyration dependences on temperature for chains (a) and for stars polymers (b); $\varepsilon > 0$ (thick lines), $\varepsilon < 0$ (thin lines). Chain length and total number of segments in stars $N = 30, 72, 120$. Horizontal dashed lines denote the limiting values of $\langle R^2 \rangle$ at $T \rightarrow \infty$.

stars $\langle R^2 \rangle (T)$ curves are of the same character as for chains though for the stars their values are smaller than for the chains with the same number of segments due to more compact structure of the stars.

Conclusion

The entropic sampling within Wang-Landau algorithm was applied for study of 3D lattice models of polymer chains and 6-arm stars. In simulations we used a semi-phantom random walk as a most appropriate reference system since in this case the fraction of self-avoiding conformations increases significantly compared to the case when phantom trajectories are used instead.[4] We shoved that the specific excess entropy of stars, rings,[5] and linear chains tends to a common limit as the chain length tends to infinity. This effect could be expected as long as with the increase of the total number of segments the relative contribution of the individual character of the structure into the specific excess entropy becomes more and more negligible.

In the thermal case we calculated energy distributions that allowed us to obtain thermodynamic properties of the studied systems in a wide temperatures range: energy, heat capacity, entropy and mean square radius of gyration. For the case of repulsive interaction ($\varepsilon > 0$), we showed that there is a single, vary smooth structural transition of all studied polymers (chains or stars of different sizes) with increasing temperature. The critical temperature of this transition is practically the same for all studied systems.

The created computer programs and obtained data provide us the basis for possible further studies: considering star polymers with longer arms and their different numbers both within lattice and continuous models; studying various cases with presence of charged groups; obtaining large information on structural properties e.g. on fluctuation characteristics of the center of mass, on the average shape of the star; studying of other non-liner systems and their complexes with linear chains etc. We hope also that results of our work could help for construction the analytical theory of star-shaped polymers.

Appendix 1

Proof of equation 3. For a semi-phantom chain the conformation with the maximum number of intersections is the square with a unit side. If N is exactly divided by 4, $N/4$ monomers are placed in each three angles of the square and $N/4+1$ are placed in the fourth angle. The number of intersections is the number of pairs in each of these nodes. In each of the first three angles we have $C^2_{N/4}$ pairs and in the fourth angle there are $C^2_{N/4+1}$ pairs. Here C^k_n (or "n over k") is the binomial coefficient, $C^k_n = \frac{n!}{k!(n-k)!}$. Therefore in this case the number of intersections is $3C^2_{N/4} + C^2_{N/4+1}$. If N is not necessarily exact multiple of 4, then N can be presented in the form $N = 4\left[\frac{N}{4}\right] + x$, where x is the residue of division of N by 4; x can have values 0, 1, 2, 3; [...] is the integer part of the number. Suppose that $N = 4\left[\frac{N}{4}\right] + 1$. For the chain of length $4[N/4]$ maximum number of intersections is $3C^2_{[N/4]}+C^2_{[N/4]+1}$. We assume that we attach a monomer to the chain of length $4[N/4]$. Attached monomer occupies the angle of the square with the number of monomers $[N/4]$ and respectively gives addition of $[N/4]$ intersections. For each next $x = 2, 3$ the contribution is similar. So we obtained the equation 3. Also we can simplify this equation:

$$
\begin{aligned}
n_{\max} &= 3C^2_{\left[\frac{N}{4}\right]} + C^2_{\left[\frac{N}{4}\right]+1} + x\left[\tfrac{N}{4}\right] = \frac{3\left[\frac{N}{4}\right]!}{2!\left(\left[\frac{N}{4}\right]-2\right)!} + \frac{\left(\left[\frac{N}{4}\right]+1\right)!}{2!\left(\left[\frac{N}{4}\right]-1\right)!} + x\left[\tfrac{N}{4}\right] = \\
&= \frac{3\left[\frac{N}{4}\right]\left(\left[\frac{N}{4}\right]-1\right)}{2} + \frac{\left(\left[\frac{N}{4}\right]+1\right)\left[\frac{N}{4}\right]}{2} + x\left[\tfrac{N}{4}\right] = \left[\frac{N}{4}\right]\left(\frac{3}{2}\left(\left[\frac{N}{4}\right]-1\right)+\frac{1}{2}\left(\left[\frac{N}{4}\right]+1\right)+x\right) = \\
&= \left[\frac{N}{4}\right]\left(\frac{3}{2}\left[\frac{N}{4}\right]-\frac{3}{2}+\frac{1}{2}\left[\frac{N}{4}\right]+\frac{1}{2}+x\right) = \left[\frac{N}{4}\right]\left(2\left[\frac{N}{4}\right]-1+x\right)
\end{aligned}
$$

Appendix 2

Proof of equation 9 for athermal part of the entropy for the star. Let us write down the number of semi-phantom conformations for the 6-arm star on the SC-lattice with total number of segments N. For generating the first segment of the first arm there exists ν positions where $\nu = 6$–the number of nearest neighbors for the SC lattice; for generation of the first segment of the second arm there remains $\nu - 1$ positions etc. The subsequent $\nu(N/\nu\text{-}1) = N\text{-}6$ segments are generated nonreversally and the number of such conformations is $(\nu-1)^{N-6}$. So the complete conformation number of the semi-phantom star with the account of the arms permutations is $\nu!(\nu-1)^{N-6}$. In order to obtain the number of SACs the complete number of semi-phantom conformations should be multiplied by normalized quantity g_0 (the share of SACs among semi-phantom chains) which is determined in the course of our computer experiment. Thus the athermal part of the entropy of the semi-phantom star is $\ln(\nu!(\nu-1)^{N-6}g_0)$. The obtained expression is transformed now in the following way:

$$\begin{aligned}
&\ln(\nu!(\nu-1)^{N-6}g_0)\\
&= \ln(\nu!(\nu-1)^{N-6}\frac{\nu^N}{\nu^N}g_0)\\
&= \ln\nu^N + \ln(\nu!\frac{(\nu-1)^{N-6}}{\nu^N}\frac{\nu}{\nu}g_0)\\
&= \ln\nu^N + \ln\left(\nu!\left(\frac{\nu-1}{\nu}\right)^{N-1}\frac{(\nu-1)^{-5}}{\nu}g_0\right)\\
&= \ln\nu^N + (N-1)\ln\left(\frac{\nu-1}{\nu}\right)\\
&\quad + \ln\nu!\frac{(\nu-1)^{-5}}{\nu}g_0\\
&= \ln\nu^N + (N-1)\ln\frac{\nu-1}{\nu}\\
&\quad + \ln\frac{(\nu-2)!}{(\nu-1)^4} + \ln g_0.
\end{aligned}$$

$\ln\nu^N$ is the entropy of phantom chain (or star) with N number of segments. So the excess entropy is

$$\Delta S_{\text{at}} = (N-1)\ln\frac{\nu-1}{\nu} + \ln\frac{(\nu-2)!}{(\nu-1)^4} + \ln g_0.$$

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