MONTE CARLO METHOD FOR STATISTICAL THERMODYNAMICS OF POLYMER CHAINS

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Self-avoiding random walks on the tetrahedral lattice were used for computer simulation of flexible polymer chains. The nearest-neighbor interaction parameter $\xi = \varepsilon/kT$ was introduced into the model. Based on the proposed method of estimation of the partition function, the mean properties of the system were calculated. It was found that the expansion of the model chains is not uniform.

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1. Introduction

Various physico-chemical properties of polymers are strictly connected with the ability of flexible polymer chains to take a large number of configurations. The knowledge of the distribution of these configurations seems to be a fundamental theoretical problem. However, theoretical analysis of the properties of polymeric system based on classical statistical thermodynamics require the introduction of numerous additional assumptions in order to simplify the problem.

In recent years numerous attempts have been made by various authors to explain some properties of flexible linear macromolecules using the computer simulation method. In these methods Monte Carlo techniques are applied to the elaboration of statistical models of polymer chains [1–4]. In this way the average properties of a model system can be calculated directly without any assumptions concerning the total density distribution of polymer segments in the coiled macromolecule.

In this paper the model of a polymer chain on the tetrahedral lattice was applied for computer simulation of flexible linear macromolecules in dilute solution. The angle between two successive linear segments of the model chain is equal to the valence angle in a tetrahedric molecule. The rotation angle around any of the segments can take three discrete values 60°, 180° and 300°. If the length of a single segment of the model chain is assumed

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to be equal to $3^{1/2}$ then the set of vectors: [1, 1, 1], [−1, 1, 1], [1, −1, 1], [1, 1, −1] [−1, −1, −1], [I, −1, −1], [−1, 1, −1], [−1, −1, 1] is a set of possible orientations of the chain segments. Thus the geometry of a linear flexible macromolecule of the polyethylene type can be satisfactory described by the model chain (see Fig. 1). Potential

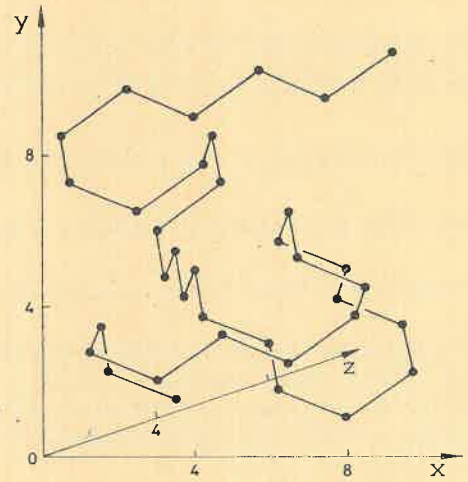

Fig. 1. Model chain on the tetrahedral lattice

of the mean force between two nonbonded (i.e. separated by more than one segment of the chain) polymer chain beads in the solution was assumed in the following form [5, 6]

$$V = \begin{cases} \infty, & r = 0 \\ \mathscr{E}, & r = 3^{1/2} \\ 0, & r > 3^{1/2} \end{cases} \tag{1}$$

where r — the distance between two nonbonded beads of the model chain, $\mathscr{E}$ — energy of interaction between two nonbonded model chain beads situated in the neighbor lattice points (energy of polymer–polymer contact in the solution). Energy of the polymer chain–solvent system was calculated as a sum of binary interactions (1).

2. *Method of computation*

The fundamental part of the computations is based on the pseudorandom generation of a large number of self-avoiding walks on the tetrahedral lattice. Each of these walks consists of a definite number of lattice beads, however they never occupy twice the same lattice point. This is the commonly used method for introducing into the model the excluded volume of the macromolecule [7–10]. The number of contacts between nonbonded beads are counted after the generation of each chain. Each bead of the model chain can participate in two such contacts. The only exception is for terminal beads where the number of contacts

can be three. Using an adequately large set of model chains of definite length a discrete distribution of end-to-end distances was obtained as well as the corresponding distribution of the number of polymer–polymer contacts.

Let the normalized discrete distribution of the end-to-end separations be described by equation (2)

$$W(R_i) = W\{i\Delta x < R \leqslant (i+1)\Delta x\} \quad \text{for} \quad i = 0, 1, 2, \ldots \tag{2}$$

where R — end-to-end separation, Δx — a small length unit (in this work Δx is assumed to be equal to 2 which is of the same range as the length of a single chain segment), $W(R_i)$ — frequency of the appearance of R in the range $(i\Delta x, (i+1)\Delta x)$ observed during simulation. For example the average value of the end-to-end separation can then be calculated from equation (3)

$$\langle R \rangle = \frac{1}{Q} \sum_{i=0}^{K} W(R_i) \cdot (i\Delta x + \Delta x/2) \cdot \exp(-\xi \cdot v(R_i)), \tag{3}$$

$$Q = \sum_{i=0}^{K} W(R_i) \cdot \exp(-\xi \cdot v(R_i)), \tag{3a}$$

where $K = R_{\max}/\Delta x$ ($R_{\max}$ — maximum observed value for the end-to-end separation), $v(R_i)$ — average polymer–polymer contact number for chains for which the end-to-end distance $i\Delta x < R \leqslant (i+1)\Delta x$, ξ — ratio of the energy of polymer–polymer contact to temperature ($\xi = \varepsilon/kT$). In a similar way other average values have been calculated.

Computations were performed in five statistical ensembles each containing 10^4 chains consisting of 15, 25, 50, 75 and 100 beads.

The presented averaging method permits one to decrease considerably the number of computations of the values of the exponential function. Thus the program is less computer time consuming. On the other hand this method is connected with the assumption that the intramolecular potential of mean force for a polymer chain in the solution can be regarded as a function of the separation between chain ends. Many theoretical works on the excluded-volume problem have been approached from this concept [11]. The approximation is satisfactory for the long chain and small energy of polymer–polymer contacts. Mean values calculated by this method are in good agreement with values calculated on the basis of an accurate partition function of the statistical sample.

3. Results and discussion

As an illustration, typical dependences between the number of polymer–polymer contacts corresponding to one chain and the distance between chain ends are presented in Fig. 2 and Fig. 3. Also the distribution of distances between model chain ends are shown on these figures. The distributions concern the case of an athermal system ($\xi = 0$). It shows that at least in the case of R values obtained with high probability the number of polymer–polymer contacts in the chain decreases linearly with the increase of the coil dimensions

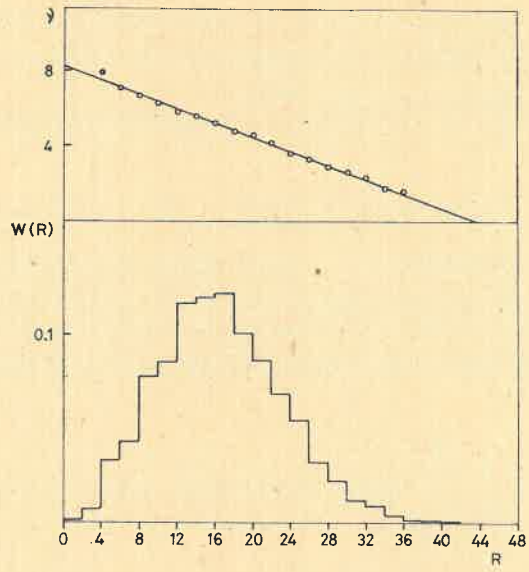

Fig. 2. Average number of polymer–polymer contacts versus the end-to-end separation and the distribution of the end-to-end separations for chains consisting of 50 beads

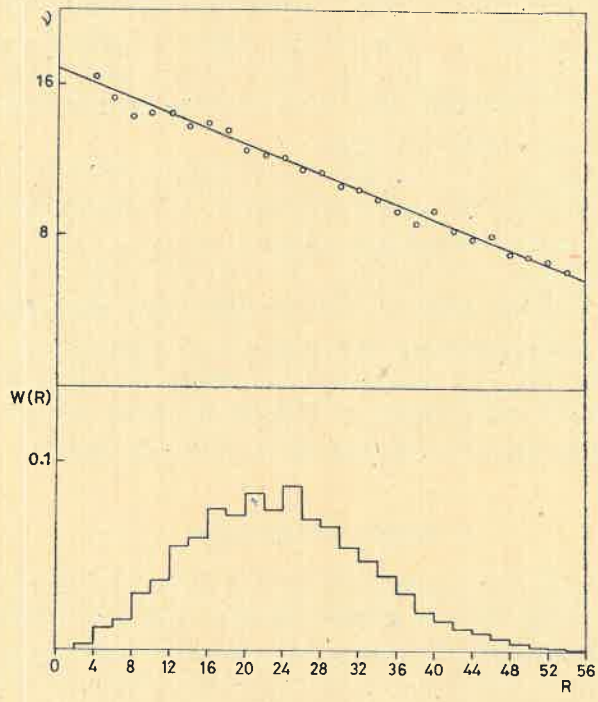

Fig. 3. Average number of polymer–polymer contacts versus the end-to-end separation and the distribution of the end-to-end separations for chains consisting of 100 beads

characterized by parameter R. These results prove that with the increase of statistical coil dimensions, the shape of the coil also changes.

The average number of polymer–polymer contacts corresponding to one segment versus model chain length is shown in Fig. 4. The curve presents the case of an athermal system and the mean value of end-to-end separation $\langle R \rangle$. For low polymerization degree

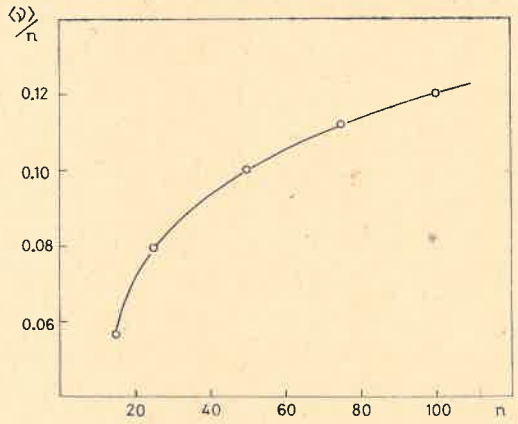

Fig. 4. Mean number of polymer–polymer contacts per one segment versus chain length for the athermal system

the contact number corresponding to one segment increases rapidly. For greater chain lengths this increase is much slower. The low contact number for short oligomers is probably connected with the limited flexibility of the model chain. On the other hand, as seen

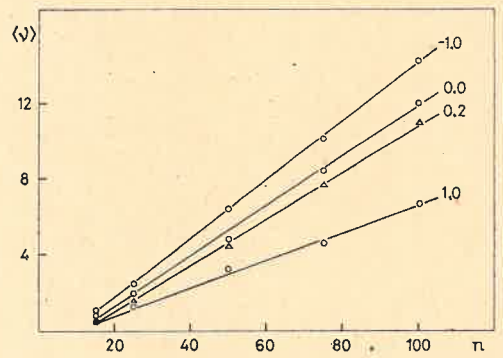

Fig. 5. Mean number of contacts in the polymer coil versus chain length for the values of ξ indicated near lines

in Fig. 5 the number of contacts corresponding to a polymer chain increases linearly with an increase of chain length. Consequently, the curve in Fig. 4 approaches asymptotically a certain level corresponding to the maximum value for average contact number per one polymer segment. For the athermal solution this value is equal to 0.133. The mean number

of polymer–polymer contacts corresponding to one segment versus the thermodynamic parameter ξ is shown in Fig. 6. Points marked in this figure correspond to the slopes of lines presented in Fig. 5. Hence the curve concerns the case of an infinitely long chain. The mean number of contacts decreases while the ξ value increases — the change is more rapid for $\xi > 0$. According to the pair potential function (1) the number of polymer–polymer contacts determines the energy of polymer chain–solvent system.

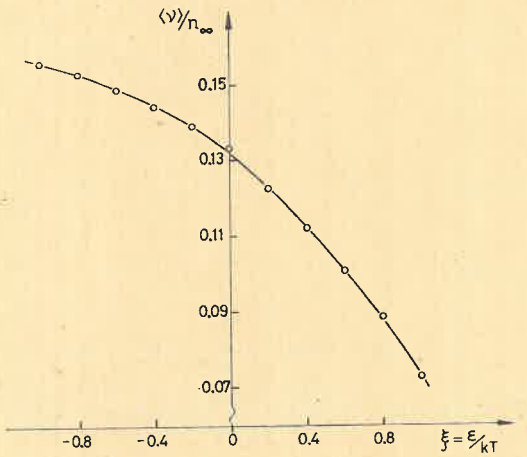

Fig. 6. Mean number of contacts per one segment versus the thermodynamic parameter ξ. The curve represents the case of an infinitely long chain

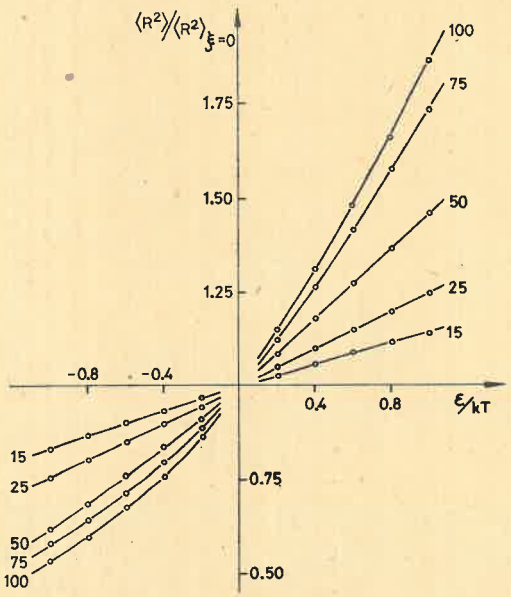

Fig. 7. Plots of the ratio $\langle R^2 \rangle$ to $\langle R^2 \rangle_{\xi=0}$ versus ξ for different chain lengths indicated near curves

The change in quality of the solvent involves a change of the mean dimensions of the polymer coil. In Fig. 7 the mean square end-to-end separation is plotted as a function of the ξ value for different chain lengths. Mean dimensions are related to those of the athermal system ($\xi = 0$). The increase of the end-to-end separation with ξ is more significant for longer chains.

4. Conclusion

The direct method of analysing statistical properties of macromolecule models presented in this paper does not contain any additional assumptions concerning the effect of the macromolecule volume on the coil. The study of the model by this method allows us to presume that the expansion of the macromolecular coil is not uniform. The main direction of coil expansion is indicated by the end-to-end vector. The intramolecular potential of the mean force for a polymer chain was observed to be a linear function of the end-to-end separation.

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