Review

COMPUTER SIMULATION OF POLYMER SOLUTION THERMODYNAMICS*

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Abstract The statistical counting method for the computer simulation of the thermodynamic quantities of polymer solution has been reviewed. The calculating results for a single athermal chain confirm the theory of the renormalization group. The results for the athermal solution are consistent with the scaling law of the osmotic pressure with the exponent 2.25. The results for a single chain with the segmental interaction are in a good agreement with the exact results obtained by the direct counting method. The results for the polymer solution show us that the Flory-Huggins parameter is strongly dependent on both the polymer concentration and the interaction energy between segments.

Keywords Monte carlo simulation; Polymer solution; Thermodynamic quantities; Translational entropy; Conformational entropy; Scaling law

INTRODUCTION

The computer simulation has an extensively application in polymer physics. The thermodynamic quantities of polymer blends, such entropy, free energy, etc., are difficult to measure experimentally, therefore the simulation calculation have a true importance for testing the theory of polymer solution. However, in the numerical simulation of polymer solution, many attentions have been given in simulating the chain dimensions, but few in calculating the entropy and the free energy due to the lack of adequate methods. K. Binder said: "Monte Carlo simulation... while the internal energy is easily calculated, neither the free energy nor entropy are obtained directly[1,2]. More than ten years ago, Meirovitch[3,4] proposed a "scanning method" to compute the entropy. Unfortunately, this approach is so far too time consuming to be of general use. Accordingly, developing a practical method seems to be still a challenge in computer simulation. Recently, we have developed a simple, convenient

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and time-saving Monte Carlo technique by which the thermodynamic quantities of a single and a multi-chain system of the random self-avoiding walk on a simple cubic lattice can be calculated.

THE CONFORMATIONAL ENTROPY FOR ATHERMAL SINGLE POLYMER CHAIN

Our method[5,6] is similar to the idea of counting walks proposed by Meirovitch. For the athermal case, the conformational entropy of a single chain of steps n is related to its conformation number $\Omega(n)$ as follows:

$$S(n) = k \ln \Omega(n) \tag{1}$$

For simplicity, k is taken as the unity of entropy so that we have $k = 1$ everywhere. For a long chain $\Omega(n)$ is very large, a direct counting seems to be impossible, but it can be calculated by our statistical counting method.

In order to test the accuracy and repeatability of the calculated results, we calculated the data of 100 groups, every group includes 10^4 samplings of chain length 1081. The average value of the conformational entropy is 1663.8, the maximum value is 1670.2 (relative deviation +0.39%), the minimum is 1660.3 (−0.2%), the mean absolute deviation is 0.09%, the root mean square deviation is 0.12%. From these data we found that the accuracy of this method is satisfactory.

Table 1 A comparison of conformational entropies of a single linear chain calculated by the statistical counting method (SCM) with the results from the renormalization group method (RG)

Chain length	Entropy: SCM	Entropy: RG	Deviation %
1201	1845.4	1854.1	−0.47
1321	2028.2	2039.4	−0.55
1441	2216.9	2224.7	−0.35
1561	2396.0	2410.0	−0.58
1681	2580.1	2595.3	−0.59
1801	2762.0	2780.6	−0.67
1921	2944.1	2965.9	−0.73
2041	3126.3	3151.2	−0.79
2101	3217.8	3243.8	−0.80

The renormalization group calculation gives the distinct number of random self-avoiding walks as

$$\Omega(n) = C_0 n^{\gamma-1} \mu^n \tag{2}$$

for large n. For a simple cubic lattice, it is quoted that the exponent γ is 7/6, μ is 4.6838[7] and C_0 is 1.17[8]. Taking the logarithm of Eq. (2) we have

$$S(n) = 1.544n + 0.1667 \ln n + 0.1570 \tag{3}$$

Owing to the disparity of results from Monte Carlo calculations, there has not reported any verification of the above equation at large value of n. The numerical results are illustrated in Table 1. We have found that the results are very close to that from the renormalization group. Table 1 also shows that the relative deviations between our method and the renormolization group method are always negative and will increase with increasing number of steps. When $n = 2101$, the deviation has a value of 0.8%. Even though, one may still consider it small.

THE THERMODYNAMIC QUANTITIES OF A SINGLE CHAIN WITH NEIGHBOUR INTERACTION[9,10]

According to the general model of neighbour interaction, when two non-connective segments were placing in the neighbourhood, a "contact" is produced. In calculating, every contact produced an energy $\Delta\varepsilon$, which can be understood as

$$\Delta\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \tag{4}$$

where ε_{11}, ε_{22} and ε_{12} are the interaction energies between segments, solvents and segment-solvent, respectively. In order to test the accuracy of the results, we calculated the conformation number of the chain length 16 at various contact numbers between the non-connective segments by direct counting. We calculated the exact values of the conformational entropy for the chain length 16 which can be taken as the criterion of testing our method and computer program. In Fig. 1, the dependence of the entropy S/k on the dimensionless parameter $\Delta\varepsilon/kT$ is given. The circles represent the simulation results obtained by the Monte Carlo method, the solid line represents the exact results. It can be found that the maximum of the entropy occurs at the athermal case (i.e. $\Delta\varepsilon = 0$). In good solvents ($\Delta\varepsilon > 0$, the non-connective segments repulse each other) the entropy decreases gradually and reach to a limitation value which corresponds to the limitation case of the maximum extension of the chain. In poor solvent, (i.e. $\Delta\varepsilon < 0$, the non-connective segments attract each other) the entropy decreases rapidly. Specially, in the region $\Delta\varepsilon/kT < -2.0$ the chain will collapse and the deviation of the simulation resulted

from the exact curve becomes very large. Thus, we can say that in the range far from the chain collapse the simulation data are consistent with the exact results very well. These results have verified our method and computer program.

In Fig. 2, the plot of the average contact number of the non-connective segments $E/\Delta\varepsilon$ vs. the parameter $\Delta\varepsilon/kT$ is given. As shown, in the athermal case ($\Delta\varepsilon = 0$) the average contact number is 2.29. In good solvent, it attends to zero eventually; and in poor solvents it increases very quickly. In the range of $\Delta\varepsilon/kT > -2.0$ the agreement between the simulation and the exact results is satisfactory.

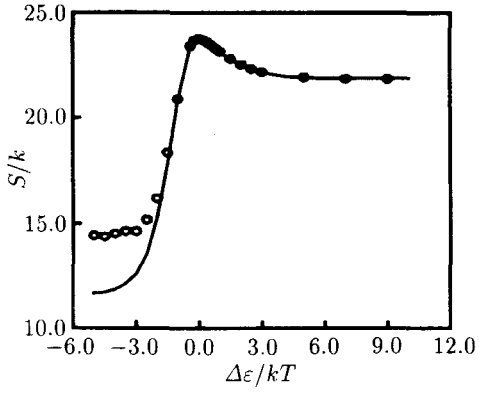

Fig. 1 The entropy per chain of the chain length 16 vs. the parameter $\Delta\varepsilon/kT$: circles: simulation, results solid line: exact results

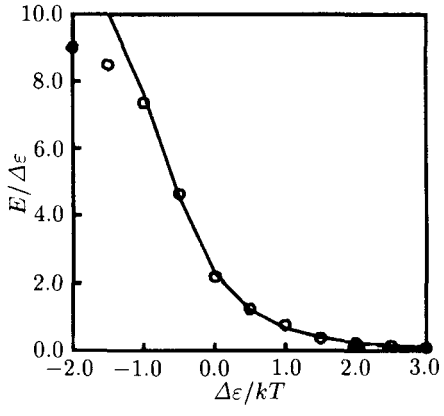

Fig. 2 The average contact number $E/\Delta\varepsilon$ of the chain length 16 vs. the parameter $\Delta\varepsilon/kT$: circles: simulation results, solid line: exact results

It is shown by these results that the influence of the segment-solvent interaction on the shape of the chain coil is very large and must be considered in both theoretical and simulation studies. In the interaction case the contact number cannot be replaced by its athermal value, otherwise a large error occurs. Unfortunately, in some works the mixing heat are regarded as proportional to the athermal contact number, the influence of the interaction on the average contact number is of no consideration. By using our method this problem can be solved.

TRANSLATIONAL ENTROPY AND CONFORMATIONAL ENTROPY[11,12]

Using the random self-avoiding walk model, it is easily found that the total entropy of multi-chain system will increase with increasing chain number. One can evaluate the contribution of each random operation to the total entropy during the

generation of chain. There are two obviously different cases to be considered here. For each polymer chain, first of all we should determine the spatial position of the chain-heads. It may be chosen randomly from all the empty sites in the whole space. In the athermal case, the possiblity of attacking each empty site should be equal, the number of the choice should be directly equal to the total number of the empty sites in the space at that time. Generally, this number is very large. The contribution of this random behaviour to the total entropy will be expressed by the multiplication of the logarithm of this method number with the Boltzmann constant k.

However, the situation becomes quite different when we decide the spatial positions of the other segments of each chain besides the first segment. For example, the second segment of each chain must be chosen only among the empty neighbour sites of the first segment of the said chain. For the self-avoiding walk chain on the simple cubic lattice, the maximum of the empty neighbour sites is only 6. It is not difficult to find that the maximum number is 5 for the third and thereafter segments of each chain. For the multi-chain system on the simple cubic lattice, this number can be calculated by the Monte Carlo method.

The contributions to the entropy are different for the two kinds of random behaviour as mentioned above. The entropies thus obtained shall behave differently in their physical properties. According to the differences between the two random behaviours, we propose that the entropy of polymer systems should be divided into two parts, i.e., translational and conformational. For the former, the position of a macromolecule can be represented by the position of its chain-head, and the entropy corresponding to the random spatial distribution of all the chain-heads can be called the translational entropy of the polymer system. This is the same as in the case of the small molecule. Therefore, the translational entropy can be described by the thermodynamics of the small molecules. In the latter case, once the positions of all chain-heads are fixed, the entropies corresponding to the possible spatial arrangement numbers of the other segments relative to their chain-heads are referred to the conformational entropy. It reflects the flexibility of the macromolecular chain and embodies the existence of the connectivity between the segments. When the molecule consists of only one segment (i.e. small molecule), the conformational entropy is absent. Hence the conformational entropy is a distinctive thermodynamic quantity of polymer. It needed to be studied by the conformational statistics. The total entropy of polymer system may be written as the summation of both terms.

example, for the random flight or 5-choice chains of length N, the conformational numbers are z^{N-1} and $z(z-1)^{N-2}$, respectively. The co-ordination number of the simple cubic lattice $z = 6$. It is easy to understand that their conformational entropies will be linearly proportional to the chain-length. The scaling feature does not exist at all. It appears that the scaling law with the theoretical exponent could be only obtained for the multi-chain systems of the self-avoiding walk on the simple cubic lattice.

FLORY-HUGGINS PARAMETER

According to Flory and Huggins theory, the mixing heat of a polymer solution is:

$$\Delta H_m = \chi \Phi (1 - \Phi) \tag{7}$$

where Φ is the volume fraction of polymer, χ is the Flory-Huggins parameter. It is subjected to many criticisms due to its discrepancy with the simulation results[15]. However, the simulation techniques in some works aren't very satisfactory. Our work[12] indicated that the scaling law of athermal polymer solution can be obtained only for the multi-chain system of the random self-avoiding walk model on the simple cubic lattice. This implies that the simulation result will be strongly dependent on the model or method used. Therefore we assert that in the simulation technique reasonable models or methods should be used, because otherwise some characters of the results can be not intrinsic, but are caused by the particularity of the unproperly used model or method.

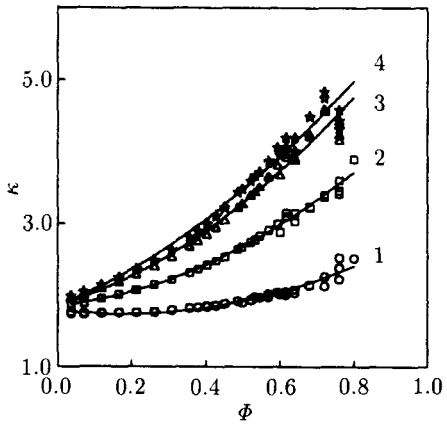

Fig. 5 The dependence of the quantity $\kappa = \Delta H_m / \{\Delta\varepsilon \Phi (1 - \Phi)\}$ on the volume fraction of polymer. $\Delta\varepsilon/kT$ are: 1: −0.3 (near Θ-solvent); 2: −0.1 (poor solvent); 3: 0.2 (good solvent); 4: 0.4 (good solvent)

It is considered that the multi-chain system of random self-avoiding walk with neighbour interaction in a periodic boundary condition on a simple cubic lattice is a good model for polymer solution. By using this model both the effect of the exclusive volume and thermodynamic interaction can be in consideration. According

to Eq. (7) we get the Flory-Huggins parameter

$$\chi = \Delta H_m / \{\Phi(1-\Phi)\} \tag{8}$$

if the quantity $\Delta H_m/\{\Phi(1-\Phi)\}$ is plotted against the volume fraction Φ, a horizontal straight line should be obtained. In Fig. 5 the dependence of $\kappa = \Delta H_m/\{\Delta\varepsilon\Phi(1-\Phi)\}$ on the volume fraction is given, where $\Delta\varepsilon$ is a constant. However, κ shows a strong dependence on both the volume fraction and the interaction parameter $\Delta\varepsilon/kT$. It is shown by our simulation results that the Flory-Huggins parameter should be a complicated function of the volume fraction Φ and the interaction parameter $\Delta\varepsilon/kT$.

It can be seen that our simulation method has the merits of high efficiency and good accuracy. One can easily find that the general self-avoiding random walk program for calculating chain dimensions can be used to compute the conformational entropy and the mixing heat data with only a small modification.

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