Monte Carlo Studies of the Volume Interactions in Macromolecules of Different Stiffness

T. M. Birshtein,* A. M. Skvortsov, and A. A. Sariban

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad 199004, USSR.

Received February 26, 1976

ABSTRACT: The behavior of macromolecules of different stiffness was studied by computer simulation. The non-self-intersecting chain on the simple cubic lattice with different probabilities of transisomers was used as a model. The quality of solvent was taken into account by the introduction of the attraction/repulsion force between each pair of the segments drawn together. It was found that the attraction energy corresponded to the theta point decreases (the theta temperature increases) with the chain stiffening. Influence of the chain stiffness on conformational characteristics (dimensions and number of the intramolecular contacts) was analyzed. A brief discussion of the nature of the coil–globule transition in flexible and stiff macromolecules is also given.

Development of the statistical mechanics and conformational statistics of individual macromolecules[1-3] had led to the facilities to compute the conformational structure of macromolecules from their chemical sequence. The object of consideration is usually a chain with the short-range intramolecular interactions only, i.e., with interactions between atoms and groups which are not far apart in sequence. In this case the complete representation of a linear conformational structure may be obtained and the chain conformations and properties can be calculated.

But in real macromolecules the interactions between groups which are remote from one another in the chain sequence always exist. Even the theta point where the effective excluded volume v_0 equals zero and a polymer chain on the average can be treated as the non-self-intersecting one is not an exclusion. The analysis of the local spatial structure of macromolecules in detail requires the long-range interactions to be taken into account. It concerns also the theta point.

In this paper we consider general regularities in the behavior of polymer chains in solution by means of the computer simulation of the model non-self-intersecting chain on the simple cubic lattice at various interaction energies between the segments in contact. We believe that model studies are the necessary steps to the direct analysis of the spatial interactions in the chains of given chemical structure,[4-7] especially as this analysis (besides the computational difficulties) is complicated by the lack of the interaction potentials of atom pairs in media (in solution).

In treatment of the volume effects in the lattice model of a non-self-intersecting chain with attraction, only flexible chains are usually considered,[8-10] the mean length of the chain rigid segment $\langle \nu \rangle$ (or the persistence length a) being approximately equal to the chain diameter d, i.e. to the lattice unit.

It is, however, well known that in real macromolecules the values of a range from several ångströms up to hundreds of ångströms. The increase of the chain stiffness does not imply in most cases an increase of the chain diameter (value of d ranges from several ångströms up to 10 Å for different polymers), i.e., in the stiff chains d/a is considerably less than that in the flexible ones.[11] The stiff chains are, consequently, effectively thinner and in such chains the interinfluence of the remote segments must be less than in flexible ones (this is confirmed by the experiment[12,13]). The change in stiffness must also lead to the change in the molecule spatial structure.

To study the influence of stiffness on the volume interactions, we considered the lattice models of chains of different stiffness,[14-16] i.e., of different ratios a/d. Growth of the ratio was due to the decrease of the probability of gauche isomers in comparison to trans ones.

Besides the impenetrability of segments the interaction of any pair of segments which are a lattice unit apart was taken into account. This value of the radius of the attraction force, the same as the chain diameter, was supposed to be constant and independent of the chain stiffness.

Lattice Chain Model

(a) Linear Structure of Chain. The chain consisting of N interacting elements joined to each other with $N - 1$ bonds of unit length was simulated on the simple cubic lattice. Each bond, starting from the second one, has five alternative directions in which it may be generated: a straight one with zero angle α with a previous bond and statistical weight t (trans isomer), and four perpendicular directions with $\alpha = \pi/2$ and statistical weight g (gauche isomers).

With the long-range interactions not being introduced, the probability of the right-angle bend of a chain linear sequence is

$$w = 4g/(t + 4g) \tag{1}$$

and the chain consists of the sequence of rigid segments with the mean number of bonds in a segment

$$\langle \nu \rangle \simeq w^{-1} \tag{2}$$

(this approximation is valid when the number of bonds in the chain is $N \gg w^{-1}$).

With increasing t/g (decreasing w) the mean length of rigid segments increases, i.e., the chain stiffness increases.

The typical feature of this model is the ability of the chain to grow in the countrary direction after a few bonds; at any stiffness there are possible two consequent bends in the same direction which yield a fold (hairpin bend) consisting of the neighbor antiparallel segments (see Figure 1). Of course, the probability of occurrence of this conformation decreases with the chain stiffness increasing.

The mean square end-to-end dimensions of the chains without long-range interactions can be expressed (the term of order $\exp(-N)$ is omitted) as follows

$$\langle h_\theta^2 \rangle / N \simeq A - B/N \tag{3}$$

$$A = 2/w - 1$$
$$B = 2(1 - w)/w^2 \tag{4}$$

The persistence length is

$$a = \langle h^2 \rangle / 2L = \langle h^2 \rangle / 2N = A/2 \tag{5}$$

(b) Parameters of the Volume Interactions in a Chain. The spatial interactions in chains were simulated by the introduction of the nonintersection of elements and the consideration of interaction between the elements in neighboring points of the lattice. Hence, the diameter of chain and the

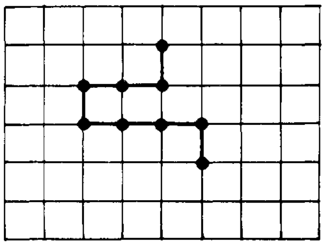

Figure 1. Hairpin bend of the chain portion.

radius of action of the force between the neighboring chain segments are equal to the lattice unit.

The interaction parameter

$$\epsilon = (F_{\mathrm{pp}} - 2F_{\mathrm{ps}})/\kappa T \qquad (6)$$

determined as the polymer–polymer (F_{pp}) and polymer–solvent (F_{ps}) contact free energy difference (in κT units) was attributed to any pair of chain elements at the distance equal to the lattice unit. As can be seen, this quantity is analogous to the Flory χ parameter[17] and is a measure of the quality of solvent in the lattice model.

At $\epsilon = 0$ the spatial interactions in a chain are merely the steric intramolecular effects, that is a chain is treated as impenetrable. It corresponds to a macromolecule in good solvent.

At $\epsilon > 0$ the polymer–solvent contact is more favorable than the intrachain contact. This leads to appearance of a solvation layer around the chain and, therefore, the growth of ϵ is equivalent to a certain thickening of a chain as well as to an increase of the interimpenetrability and, consequently, an increase of the solvent quality. In the limit $\epsilon \to \infty$ the impenetrable chain of doubled diameter is to be dealt with.

At $\epsilon < 0$ the intrachain contacts are more favorable than the polymer–solvent ones and growth of $(-\epsilon)$ corresponds to the deterioration of solvent. At certain value $\epsilon_\theta < 0$ the additional intrachain contacts merely compensate effects connected with the chain thickness and this corresponds to the unperturbed coil in the theta point.

At $-\epsilon > -\epsilon_\theta$ the chain structure becomes more compact than in the theta point, that is an isolated chain carries out the coil–globule transition.[14,18] The computer simulation of this transition by means of the lattice model reveals that the flexible chains are being gradually compressed by the intramolecular attraction, forming a compact globule, and the stiff chains, with the rigid segment being sufficiently long, form crystallike folded structures as a result of the "all-or-none" transition.[14,15]

All mean conformational characteristics of model chains were calculated by the Monte Carlo technique. The ensemble with given N and t/g was generated, the number of chains being not less than 4000–5000, and all characteristics of chains at every value of ϵ were averaged over it. The computations were carried out on the BESM-3M and BESM-6 computers and the procedure was similar to that employed elsewhere.[14]

Results and Discussion

Dependence of ϵ_θ on the Stiffness of Chain. To consider the quantity ϵ_θ corresponding to the theta conditions for model chains we take as a criterium of the theta point the coincidence of the calculated dependence $\langle h^2 \rangle/n$ on $1/n$ and the theoretical ones for the unperturbed chains (eq 3 and 4).

Figure 2 shows the results for the flexible ($w = 4/5$) and semirigid ($w = 1/4$) chains. Values ϵ_θ derived from them are listed in Table I. It should be noted that the lattice model used provides only general dependence of ϵ_θ on the parameters of the system and the numerical values of ϵ_θ cannot be directly connected with real macromolecules. As is seen from Table I the increase in stiffness of macromolecules leads to the displacement of the theta point to less absolute values of the attraction energy $|\epsilon_\theta|$, that is to the shortening of the range of solubility ($-\epsilon < -\epsilon_\theta$). The obtained dependence of ϵ_θ on the stiffness of chain can be approximately expressed as follows (see Figure 3).

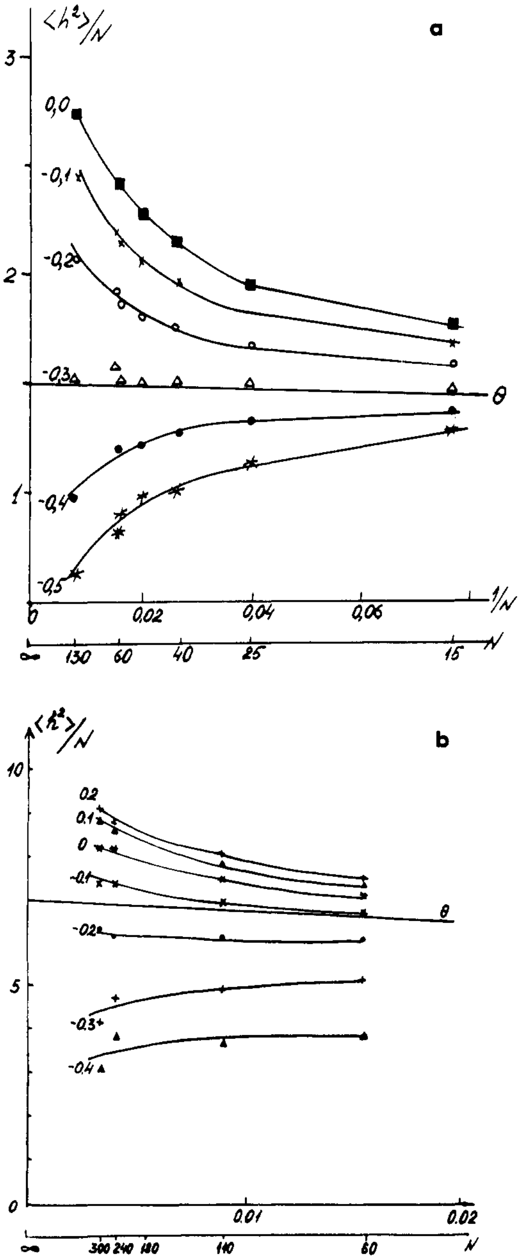

Figure 2. A plot of the end-to-end dimensions as a function of the number of bonds: (a) flexible chains with $w = 4/5$; (b) semirigid chains with $w = 1/4$.

$$\epsilon_\theta \simeq -(a + 2.5)^{-1} \qquad (7)$$

The origin of the dependence of ϵ_θ on the stiffness of chain can be easily understood. Indeed, as has been emphasized, the chains which demonstrate an increase of stiffness with the chain diameter being fixed are treated. Therefore, d/a decreases with increasing a. In the limit $d/a \to 0$ we have a spatialless chain which, therefore, is in theta conditions at the interaction energy $\epsilon_\theta = 0$. The increase of d/a, i.e., the decrease of the chain stiffness, is equivalent to the effective growth of the chain diameter. Furthermore, the steric effects grow and

Table I
Parameters of the Chains Studied

w	$\langle \nu \rangle$	A	B	$L_{\max}$	$L_{\max}/a$	a/d	$-\epsilon_\theta$
$4/5$	1.25	1.5	$5/8$	128	100	0.75	0.3
$1/2$	2.0	3	4	100	50	1.5	0.25
$1/4$	4.0	7	24	300	75	3.5	0.15
$1/8$	8.0	15	116	343	40	7.5	0.1

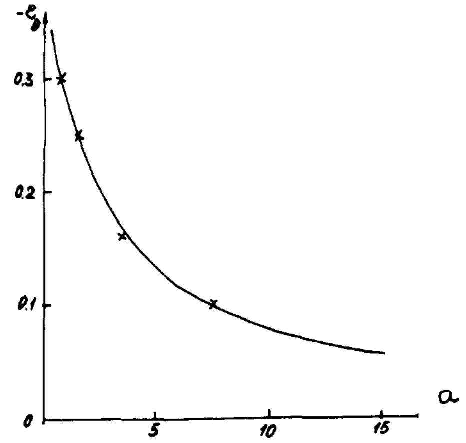

Figure 3. The attraction energy ϵ_θ corresponded to the theta point as a function of the chain stiffness. The solid curves correspond to the empirical eq 7, and the points represent the Monte Carlo results.

greater values of the attraction energy $-\epsilon$ are needed to compensate them.

Since ϵ is taken in κT units (see eq 6), the decrease in ϵ_θ is equivalent to the increase of theta temperature and, therefore, the increase of the stiffness of macromolecule (its chemical structure being invariable) must be accompanied by the growth of the theta temperature of the polymer–solvent system. A quantitative treatment of the dependence of ϵ_θ on d/a can be found elsewhere.[11]

Difference in the flexibility of polymers of the same chemical structure can be demonstrated on several objects, such as, for example, polymers of different stereoregularity, in particular, iso- and syndiotactic polymers. Moreover, polybutene shows an increase of theta temperature with increasing chain stiffness.[19] The similar growth of theta temperature may be expected if we deal with the ladder polymers instead of the linear ones of the same chemical nature (e.g., ladder and linear polysiloxanes). It should be pointed out that, generally speaking, polypeptide and polynucleotide molecules undergoing the helix–coil transition change the nature of interaction with solvent because of the break of the hydrogen bonds. Hence, the change in ϵ_θ following from our calculations cannot result in the change of theta temperature only. In the beginning of denaturation where the degree of denaturation is small the chemical structure may be treated as invariable. At the same time the change of temperature or solvent in this region alters sharply the chain dimensions because new bends appear, and this must lead to the change of theta temperature of the system.

Dimensions of Macromolecules

Figure 4 shows the mean dimensions of flexible $w = 4/5$ ($a = 0.75$, $L = 60$) and stiffer $w = 1/4$ ($a = 3.5$, $L = 300$) chains consisting of the same number of Kuhn segments $L/2a \simeq 40$ vs. the intramolecular interaction parameter ϵ. One can see that when the intramolecular attraction energy $-\epsilon$ increases the chain dimensions decrease. If the behavior of stiff chains were similar to that of flexible ones, then the ratio $\langle h_2^2\rangle/\langle h_1^2\rangle$ would not depend on ϵ. At the same time, as Figure 5 shows, the dimension ratio for chains of different stiffness depends on the quality of solvent. In good solvents when $-\epsilon < -\epsilon_\theta$ it is less than the ratio for their unperturbed dimensions

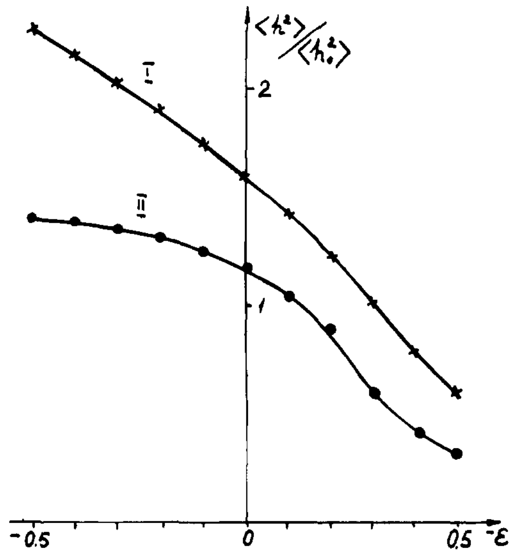

Figure 4. End-to-end dimensions of flexible (I) and stiff (II) chains vs. the intramolecular interaction parameter ϵ. (I) $a_1/d = 0.75$, $L_1 = 60$; (II) $a_2/d = 3.5$, $L_2 = 300$.

$$\langle h_2^2\rangle_\theta/\langle h_1^2\rangle_\theta = L_2a_2/L_1a_1 = (a_2/a_1)^2 \simeq 23 \qquad (8)$$

As has been noted, this is connected with greater spatial interaction in the flexible chains than in stiff ones. This effect is also demonstrated in Figure 4, where the dimensions of stiff chains change weakly in the repulsion region. Diminution of the ratio $\langle h_2^2\rangle/\langle h_1^2\rangle$ in the right side of Figure 5 (in the intramolecular attraction region) can be explained by the increase of density of segments in the region of the coil–globule transition. Dimensions of the close-packed globules show only weak dependence on the number of chain segments.

Intramolecular Contacts

Differences between the properties of flexible and stiff chains can also be manifested by the dependence of the mean number of contacts of a segment $\langle m\rangle/L$ on solvent ($\langle m\rangle$ is the total number of contacts in the chain). If each segment has on the average one contact with some segment then $\langle m\rangle/L = 0.5$. In the model used the maximum value $\langle m\rangle/L = 2$ corresponds to the close-packed infinite chain.

It is natural that the mean number of contacts in stiff chains in the repulsive region is less than in flexible chains (see Figure 6). It is interesting to note that in region $-\epsilon < 0$ the value $\langle m\rangle$ is also less, though, as mentioned above, the total number of segments in the stiff chain is five times higher than in the flexible one (at the same value L/a).

On the other hand, in the region of great attraction $-\epsilon > -\epsilon_\theta$ where solvent is poorer than in the theta point, the mean

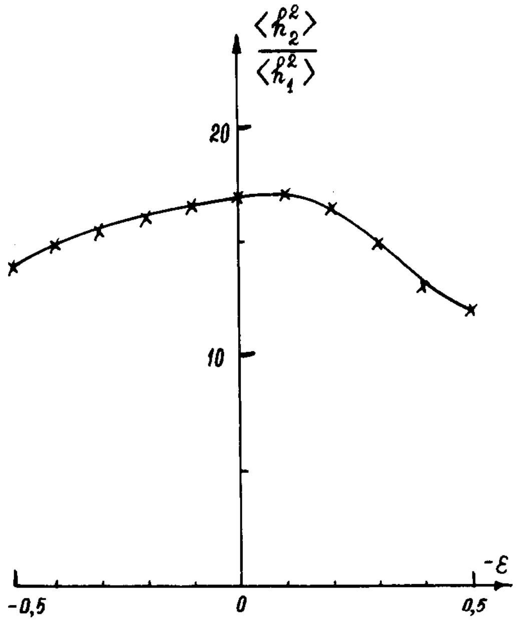

Figure 5. The dimension ratio for stiff and flexible chains as a function of the intramolecular interaction parameter ϵ.

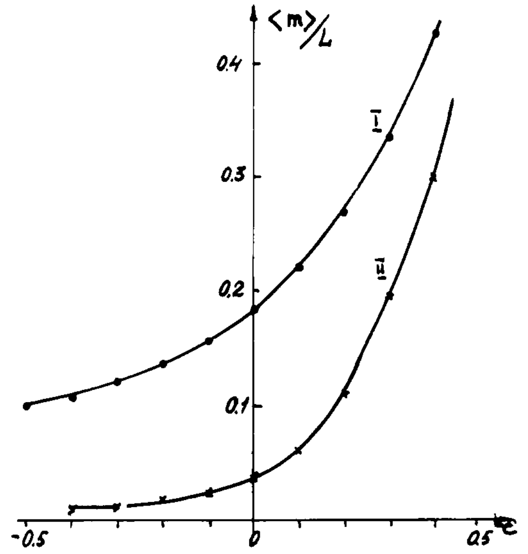

Figure 6. The mean number of contacts of the chain segment vs. the intramolecular interaction parameter ϵ: (1) flexible chains with $a_1/d = 0.75$, $L_1 = 60$; (2) stiffer chains with $a_2/d = 3.5$, $L_2 = 300$.

number of contacts sharply grows in a stiff chain. Obviously, in both cases the great intramolecular attraction leads to the formation of compact structures. But as found previously by means of Monte Carlo computation[14] (see also[15]), flexible and stiff chains differ both in the character of transition and final states. While the flexible chains, even being rather long (consisting of several hundred segments of $N = 343$), are gradually squeezed by the intramolecular forces into the more and more compact structureless globule, characterized by a rather great entropy, the stiff chains, even consisting of a few segments (about 10), form crystallike folded structures which are "unique" in the sense that contributions of their entropies to the free energy are negligible. At the same time the transition from the coil state into the quasi-crystalline one is "all-or-none" transition, i.e., the first-order one, without a number of intermediate states (the intramolecular energy distribution function is two-hump shaped).

Thus, the macromolecules with great local asymmetry are dispersed in solution in the coil state, with the coil dimensions and properties weakly depending on solvent. The intramolecular condensation results in the crystallike structures. On the contrary, the flexible chains (i.e., polymers with small local asymmetry), with the chain diameter and dimensions of rigid segment being of the same order (irrespective of the segment dimensions), form the coil with many contacts expanded by the spatial effects; this coil gradually diminishes with the solvent quality deteriorating.

As mentioned above this conclusion is based directly on the "computer experiment" data, i.e., on the form of the intramolecular energy distribution function for the chains of finite length.[14,15] Their results are of interest because of some disagreement between the theoretical suggestion[20–26] about the nature of coil–globule transition in infinitely long flexible chains (first- or second-order phase transition or cooperative transition).

References and Notes

(1) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains", Interscience, New York, N.Y., 1963.
(2) T. M. Birshtein and O. B. Ptitsyn, "Conformations of Macromolecules", Interscience, New York, N.Y., 1966.
(3) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(4) S. Tanaka and A. Nakajima, *Macromolecules*, **5**, 708, 714 (1972).
(5) M. Lal and D. Spencer, *Mol. Phys.*, **22**, 649 (1971).
(6) M. Lal and D. Spencer, *Mol. Phys.*, **26**, 1 (1973).
(7) K. K. Knael and R. A. Scott, *J. Chem. Phys.*, **54**, 566 (1971).
(8) F. T. Wall, S. Windwer, and P. J. Gans, *J. Chem. Phys.*, **38**, 2222, 2228 (1963).
(9) J. Mazur and F. L. McCrackin, *J. Chem. Phys.*, **49**, 648 (1968); J. Mazur, *Adv. Chem. Phys.*, **15**, 261 (1969)
(10) F. L. McCrackin, J. Mazur, and C. M. Guttman, *Macromolecules*, **6**, 859 (1973).
(11) T. M. Birshtein, A. M. Skvortsov, and A. A. Sariban, *Macromolecules*, submitted.
(12) R. G. Kirste, *Discuss. Faraday Soc.*, **No. 49**, 51 (1970).
(13) V. N. Tsvetkov, *Usp. Khim.*, **38**, 1647 (1969).
(14) A. M. Elyashevich and A. M. Skvortsov, *Mol. Biol.*, **5**, 204 (1971).
(15) T. M. Birshtein, A. M. Elyashevich, and L. A. Morgenstern, *Biophys. Chem.*, **1**, 242 (1975).
(16) T. M. Birshtein, A. A. Sariban, and A. M. Skvortsov, *Vysokomol. Soedin., Ser. A*, **17**, 1962 (1975).
(17) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, 1953.
(18) A. K. Kron, O. B. Ptitsyn, A. M. Skvortsov, and A. K. Fedorov, *Mol. Biol.*, **1**, 576 (1967).
(19) W. R. Krigbaum, "Newer Methods of Polymer Characterisation", B. Ke, Ed., Interscience, New York, N.Y., 1964, p 9.
(20) O. B. Ptitsyn and Yu. E. Eizner, *Biofizika*, **10**, 3 (1965).
(21) I. M. Lifshits, *Zh. Eksp. Teor. Fiz.*, **55**, 2408 (1968).
(22) Yu. E. Eizner, *Vysokomol. Soedin.*, **11**, 364 (1969).
(23) C. Domb, *Polymer*, **15**, 259 (1974).
(24) A. R. Massih and M. A. Moore, *J. Phys. A: Math., Nucl. Gen.*, **8**, 237 (1975).
(25) R. Finsy, M. Janssens, and A. Bellemans, *J. Phys. A: Math., Nucl. Gen.* **8**, L106 (1975).
(26) T. Morita, *J. Phys. A: Math., Nucl. Gen.*, **9**, 169 (1976).