Conformer populations and the excluded volume effect in lattice simulations of flexible chains in solutions

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Monte-Carlo simulations on a tetrahedral lattice have been used to investigate whether a change in solvent quality induces *gauche–trans* conformational isomerization in the chain backbone. The populations of *gauche* states x_g and of the all-*trans* sequences with length i bonds were calculated. The results show that the conformational equilibrium is affected by a solvent mainly in the short and flexible chains. The actual amount of solvent perturbation depends critically on the severity of intramolecular excluded volume interactions assumed in the lattice chain models. In discussion, a general neglect of this effect in the literature is pointed out which, in the light of the present study, seems to be warranted for long and semiflexible chains only.

(Keywords: Monte-Carlo simulations; conformational statistics; excluded volume effect; solvent-induced chain expansion)

INTRODUCTION

Rotational isomeric theory (RIS) has achieved considerable success in rationalizing configuration-dependent physical properties of macromolecules unperturbed by long-range interactions[1]. Two kinds of parameters enter the RIS theory: geometrical parameters of the chain backbone, and the short-range ('local') interactions between atom groups separated by three or four bonds. 'Non-local' interactions of groups separated in the chain backbone by five or more groups are neglected in the RIS model. The computations by the matrix RIS theory give the mean-square end-to-end distance $\langle R^2\rangle_0$, the mean square of the dipole moment of the monomer $\langle\mu^2\rangle_0$ and other conformation-dependent quantities in good accord with values measured under theta conditions. RIS calculations also provide the quantities characterizing the conformational equilibrium in a chain, such as the molar fractions of the *trans* (t) or *gauche* (g) conformations x_t and x_g (the first-order probabilities of the occurrence of bonds in a given state[1]), or the molar fractions of bond pairs of the type x_{tt}, x_{tg}, etc. (the second-order probabilities). To date, relatively little attention has been paid in the literature to the comparison of computed and measured populations of conformers in the polymer chains.

Much effort has been concentrated on the question of the degree to which the conformation-dependent properties are affected by perturbations produced by intrachain long-range excluded volume (EV) interactions. The term 'long-range' in this context applies to groups widely separated along the chain contour but able to come close to each other due to the chain flexibility. In most cases the 'unperturbed' quantities are considerably affected by EV interactions; a prominent example is the expansion of the mean dimensions of chains expressed by the expansion coefficient $\alpha^2 = \langle R^2\rangle/\langle R^2\rangle_0$. However, in some cases investigated in detail by Mattice[2–4], a negligible effect of EV was reported on values of $\langle\mu^2\rangle_0$ and on some optical conformation-dependent quantities.

The present paper addresses the unresolved question of whether there is (and if so how large) an influence of EV interactions on the conformer populations in a macromolecule. In the standard approach, only the variation of the conformer population by temperature is presumed and the change of the population with the EV effect is only exceptionally invoked[5,6]. An extension of the RIS theory to the chains perturbed by EV interactions[5] was based on the assumption that the first-order populations (x_t, x_g) in molecules such as polymethylene, are unaffected by the EV interactions; the chain expansion in good solvents is a consequence of the enhanced populations of the x_{tt} pairs and of the longer all-*trans* sequences. In contrast, an opposing view was advocated[6] which assumes alterations in the first-order populations x_t in good solvents relative to the theta state.

Lattice and off-lattice Monte-Carlo (MC) simulations are methods of choice to find whether the expansion of macromolecules in good solvents is connected with the rotational isomerization in the chain backbone. MC simulations are a popular tool to study various polymer properties; however, the conformer populations have seldom been evaluated[7]. The proper modelling of intramolecular EV interactions in lattice simulations is still a matter of discussion. In the first approach, the sum of all non-local interactions (interactions of groups separated by more than four bonds) is identified with the intramolecular EV effect[8,9]. Additionally, by assuming a hard-core repulsion between interacting groups, the first-neighbour sites to a site occupied by a reference chain are excluded. In this way, the chain 'thickness' is accounted for in simulations.

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In the second approach, the EV effect is identified only with a part of the non-local interactions, namely, with interactions between the groups separated, for example, by eight and more bonds[4]. Such a treatment of EV is supported by an analysis[10] claiming that a small fraction of non-local interactions actually contributes to the value of the unperturbed dimensions.

In this paper, the variation of the conformer populations by EV interactions has been investigated by MC simulations on a tetrahedral (diamond) lattice for chains of variable length and flexibility. We have found that the results are sensitive to the method of incorporation of 'local' interactions and of the EV effect in the calculations. By neglecting the 'thickness' of the chain and the 'pentane effect', the population of the *gauche* conformations x_g in the molecule backbone changes by several per cent in short and flexible chains. In contrast, the population of x_g remains almost constant with coil expansion in longer, semiflexible chains after explicit considerations of chain 'thickness' and the 'pentane effect'.

METHOD

Self-avoiding chains with lengths of 20 and 100 segments were generated on a diamond lattice by a standard procedure[7]. The conformational states *trans* (t), and *gauche* (g^+ and g^-) with torsional angles of 0°, 120° and −120°, respectively, can be defined on a diamond lattice in analogy with the situation in real macromolecules of the alkane type. The chain flexibility was varied through the parameters ε_g and ω. The first parameter, ε_g, is related to the *gauche–trans* energy difference Δe_g by the relation $\varepsilon_g = \Delta e_g/RT$. The second parameter, ω, regulates the suppression of bond pairs in the chain backbone with the two adjacent *gauche* bonds of the opposite sign such as g^+g^- (the 'pentane effect'; *Figure 1a*). The

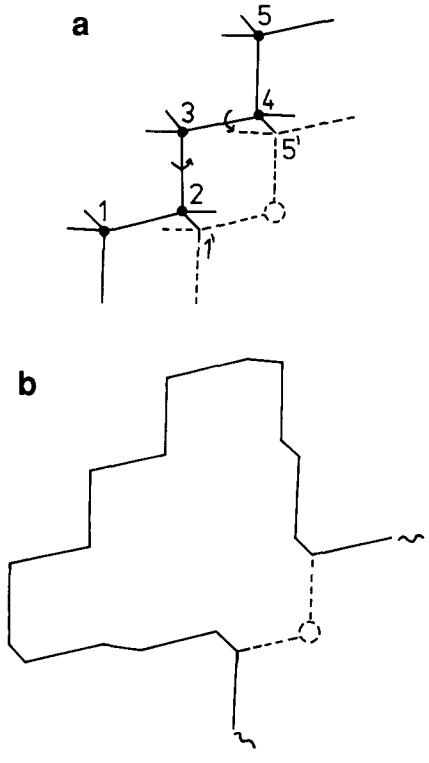

Figure 1 Representations of local and non-local interactions on a tetrahedral lattice: (a) the pentane effect; (b) the long-range loop of a chain with an inaccessible first-neighbour site

expansion or contraction of a macromolecule due to the intramolecular EV effect was modelled through the parameter $\varepsilon_s = e_{ij}/RT$ which accounts for non-local repulsion or attraction between the ith and jth groups separated by more than four bonds.

In simulations, the lattice spacing $l = 3^{1/2}$ was assumed for a diamond lattice which corresponds to the lattice spacing $l' = 1$ on a conjugate cubic lattice. Calculations were made for two models, A and B, differing in the parameters of local interactions as well as in the extent of inclusion of EV interactions. Model A is frequently used[7,11] in theoretical treatments of the excluded volume by lattice calculations. In this model local interactions are governed by the relative energy ε_g only; the pentane effect is neglected ($\omega = 1$). Self-avoiding chains are generated using the unoccupied sites, including the first-neighbour sites to a reference chain on a lattice. The first-neighbour contacts and their energy (related to the parameter ε_s) determine the EV effect in model A.

In model B, the pentane effect is taken into account in local interactions by assuming $\omega = 0$. That means that for all the segments i and j separated along the chain by four bonds, the conformations for which $\langle R_{ij}^2 \rangle \leqslant 8$ are neglected in the simulations (*Figure 1a*). In addition, in model B stricter conditions are introduced for long-range steric interactions[8,9]. Hard-core repulsion between non-bonded groups is assumed, which may be regarded as a 'covolume' or the 'width' of a macromolecule. In lattice calculations, the hard-core repulsion is converted into the condition that the occupation of the first-neighbour site next to a given chain is forbidden, only second-neighbour sites being accessible (*Figure 1b*). The second-neighbour site to a given site on a diamond lattice is best visualized by the placement of two opposite CH_2 groups in a chain conformation of cyclohexane. In other words, the condition of inaccessibility of the first-neighbour sites corresponds in the paraffinic molecules to a cut-off distance of about 0.25 nm for the hard-core repulsion of the CH_2 groups. The full analogy with the assumption $\omega = 0$ for local interactions (see *Figure 1a*) would require that even second-neighbour sites should be inaccessible. However, we feel that in this respect the two cases are not equivalent since the lattice simulations do not consider the accumulations of small fluctuations of valence parameters in the long loops that make second-neighbour contacts possible. The contact energy $e_{i,j}$ is calculated in model B through second-neighbour pairs.

In simulations, up to 6×10^7 reptation moves were applied, depending on the statistics. Smaller samplings were needed for the short expanded chains in model A and longer runs were used for the long chains in the collapsed state in model B. The Metropolis acceptance ratio was in the range 0.1–0.7. The *trans* and *gauche* conformers and the next-neighbour sites were identified by the geometry condition $\langle R_{ij}^2 \rangle = 19$, 11 and 8, respectively, where i, j are corresponding sites representing either of three conformations between these sites. (This is easily discernible from a drawing of two conjugate lattices: cubic and tetrahedral. Starting from the centre of the cubic unit the first tetrahedron is formed by going to four corners of the cube.) The fractions $p(i)$ of the *trans* conformers present in a chain in a sequence of i bonds were also evaluated. The mean-square end-to-end distance was calculated as usual[12]. Even though the conformational sampling was done using the conjugate

cubic lattice representation with integers 19, 11 and 8, mentioned above, for convenience the mean chain dimensions $\langle R^2 \rangle$ henceforth refer to the tetrahedral lattice spacing $l = 1$.

RESULTS

We have investigated the variation of the concentration of the *gauche* conformers x_g in macromolecules as a function of (a) the chain length, (b) the chain flexibility expressed through the relative conformational energy ε_g and (c) the severity of EV interactions as in model A or B. Calculations were made for two chain lengths, $N = 20$ and 100. The two values, 0 and 1, were selected for the parameter ε_g and are shown in parentheses in the specification of the model, e.g. A(0). The choice of the relative intersegmental energy ε_s, from about -3 to 3, regulates the coil expansion or contraction. In this way, the parameter ε_s serves as a measure of the thermodynamic quality of the solvent (or the temperature).

The conformer populations were sampled over the entire range of macromolecular size, from expanded coils to compact collapsed coils. The variation of the mean dimensions of the chain $\langle R^2 \rangle$ with the contact energy parameter ε_s is shown in *Figure 2* for the two chain lengths and for four combinations of the model and the parameter ε_g. It is seen that already a value of $\varepsilon_s \approx 2$ is sufficient to expand the coils almost to the ultimate degree. It is evident from *Figure 2* that inclusion of the pentane effect and of the chain thickness considerably increases the chain dimensions at the specified value of ε_s. A similar trend is brought about through reduction of the chain flexibility by changing ε_g from 0 to 1 in both models A and B.

In *Figure 2*, at first the gradual decrease of the chain dimensions is observed by an alleviation of intersegmental repulsion. Subsequently, in the range of intersegmental attraction, an abrupt decrease of the coil size into a collapsed state takes place. For $N = 100$ all four curves in *Figure 2b* converge in the vicinity of $\varepsilon_s = -1$; that is, in the collapsed state almost all differences in the treatments of the chain flexibility and/or EV interactions are immaterial. The statistics of simulations deteriorates considerably in the region of the collapsed state and so does the scatter of data. This observation is apparently connected with the fact that the collapsed chains may produce a variety of densely packed structures with folded chains[7].

The chains generated for the specified parameter ε_s can be characterized by some averaged value of the *gauche* conformer concentration x_g. Accordingly, the plots in *Figure 2* were transformed onto the related graphs of the mean dimensions of chains *versus* the population of the *gauche* conformation x_g (*Figure 3*). As expected, the model A(0) with flexible chains gives the maximum values of x_g, in the range between 0.6 and 0.7. The fraction x_g is slightly reduced in the longer chains ($N = 100$) relative to shorter chains ($N = 20$) for otherwise equal model parameters.

In almost all cases shown in *Figure 3* a linear function between the dimensions $\langle R^2 \rangle$ and the population x_g was found. The gradual expansion of a polymer coil from the collapsed state is accompanied by an increase of the extended *trans* conformation and the population x_g is

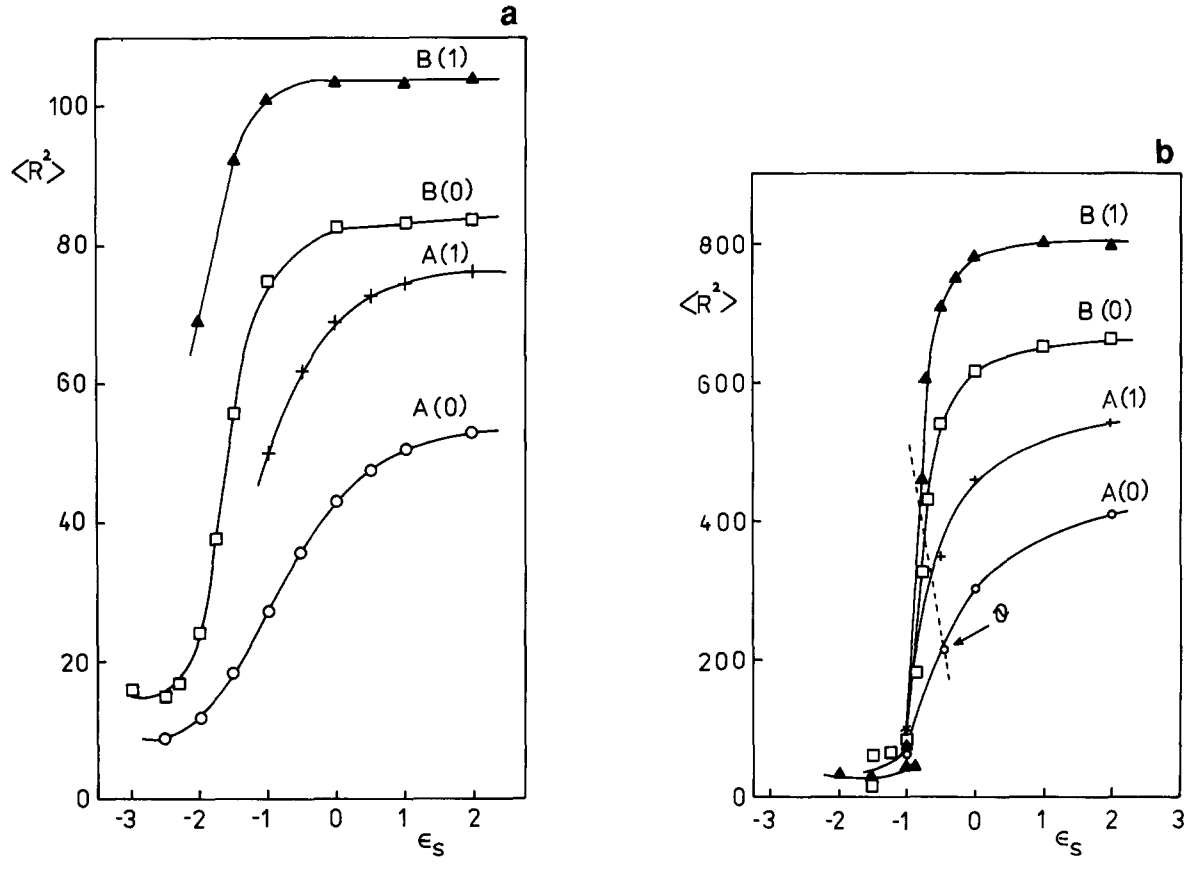

Figure 2 Variation of mean dimensions $\langle R^2 \rangle$ with relative intersegmental energy ε_s for the four different models and chain lengths of (a) 20 and (b) 100 segments. In (b), the arrow indicates the theta point on the A(0) curve, and the dashed line approximates the theta points in the remaining three models (see text)

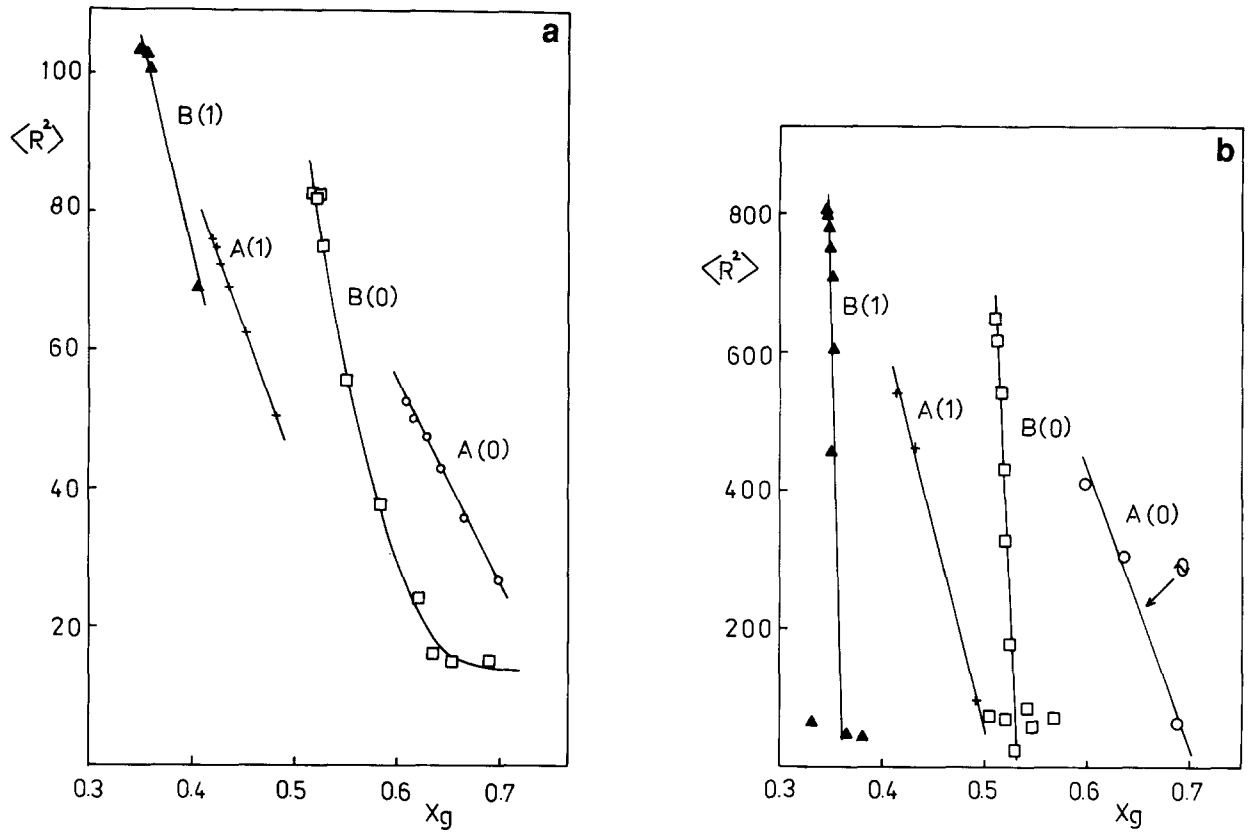

Figure 3 Variation of mean dimensions $\langle R^2 \rangle$ with fraction of *gauche* conformers x_g for the four different models and chain lengths of (a) 20 and (b) 100 segments. In (b), the arrow indicates the theta point on the A(0) curve.

reduced. The rather large scatter already mentioned allows only an approximate drawing of the curves in the region of the collapsed state. The slopes of the linear parts of the curves shown in *Figure 3*, denoted as γ, are listed in *Table 1*. It is evident that the magnitude of γ is primarily influenced by the method of inclusion of the EV effect in model A or B. For example, the slopes γ in *Figure 3* for both chain lengths in model A(0) show that the transition from a collapsed into a fully expanded coil is accompanied by more than a 10% reduction in the population of the coiled *gauche* conformations. A slightly less distinct reduction of x_g was observed for model A(1). In contrast, model B provides values of γ several times smaller for the long chains than in model A, indicating only limited *gauche–trans* isomerization by coil swelling.

The expansion coefficient α, related to the dimensions of a coil in the theta state, is a convenient measure of chain expansion due to EV interactions. Hence, representation of the coefficient α as a function of the fraction x_g is useful. In MC calculations, theta conditions are simulated by a proper choice of the parameter ε_s in the range of attractive intersegmental interactions. The actual value of ε_s depends on the type of lattice, interaction potential, chain length, etc. For the models used in the present paper, only the value of the theta state for the chains generated on a tetrahedral lattice with the parameters of model A(0), $\varepsilon_s = -0.4634$, is available from the literature[11]. The arrows in *Figures 2b* and *3b* mark the corresponding theta points.

The data for model A(0) in *Figure 3* were converted into a related function of α^2 *versus* x_g using the above-mentioned value of ε_s for the calculations of the unperturbed dimensions $\langle R^2 \rangle_0$ (*Figure 4*). Because of the lack of data on the ε_s parameters for the theta state, only an approximate procedure was used in a similar conversion of the remaining three curves in *Figure 3*. Arbitrarily, we assigned the reference dimensions $\langle R^2 \rangle_{ref}$ to the intersections of the three curves in *Figure 2b* and a straight line traversing the theta point on the A(0) curve. We have assumed that in all four cases the theta points are located close to the inflection points of the curves in *Figure 2b* and thus the reference dimensions should approximate the unperturbed dimensions fairly well. The expansion coefficient α^2_{rel}, defined by analogy with the coefficient α^2, was evaluated for the remaining models A(1), B(0) and B(1) and is plotted in *Figure 4* as a function of x_g.

Similarly to *Figure 3*, a linear decrease of the *gauche* population with the degree of coil swelling is observed in *Figure 4* with the slopes γ^* listed in *Table 1*. Again, the qualitative difference in the sensitivity of the conformer population to the solvent quality between

Table 1 Slopes of the straight lines from *Figures 3* and *4*, γ and γ^*, respectively, as indicators of sensitivity of the conformer populations x_g to solvent quality for the four different models

	$N = 20$		$N = 100$	
	$-\gamma$	$-\gamma^* \times 100$	$-\gamma$	$-\gamma^* \times 100$
A(0)	289	12.8	4050	5.4
A(1)	401		5850	5.5
B(0)	870[a]		32 500	1.2
B(1)	600		53 333	0.8

[a] From the linear part of the curve

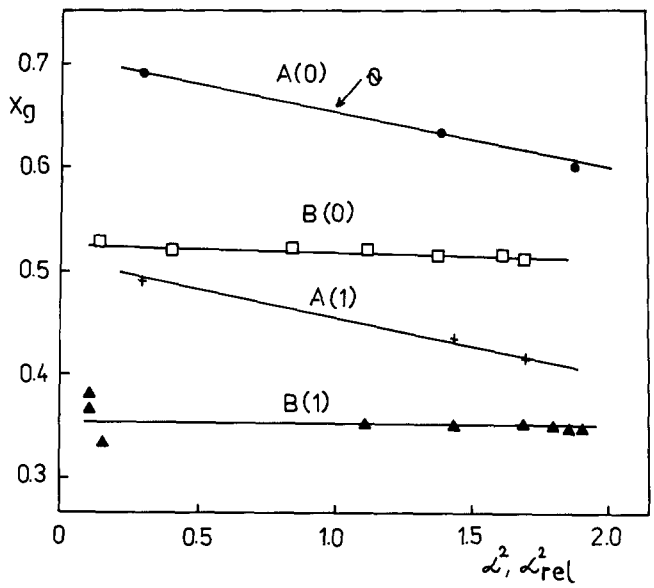

Figure 4 Variation of the fraction of *gauche* conformers x_g with the square of the expansion coefficient α and of the related coefficient α_{rel} (see text) for the four different models and chain length of 100 segments. The arrow indicates the theta point on the A(0) curve

models A and B is apparent. For the short, flexible chains and model A, changes in the population x_g by several per cent are predicted on the transition of a coil from a poor to a good solvent.

The intramolecular EV interactions may also affect, apart from the first-order probability x_g, the higher-order probabilities of the occurrence of the longer sequences of bonds. We have enumerated the distribution of the all-*trans* sequences for the three representative cases: in good solvents, in the vicinity of the theta state and close to the collapsed state. *Figures 5a–c* show typical examples of the sequence statistics: the fractions of the all-*trans* sequences of length *i*-bonds for models A(0), A(1) and B(0), respectively. The largest enhancement of the population of the all-*trans* sequences of the type ...*tttt*... with the solvent quality is found again in model A. This enhancement is discernible in the sequences up to eight or nine bonds. The reduced chain flexibility in model A(1) makes the probability of the population x_{tt} even more likely than the probability of x_t and the longer sequences become slightly more favoured relative to model A(0) (*Figure 5b*). The quality of the solvent seems to play a minor role in the sequence distribution calculated by model B(0).

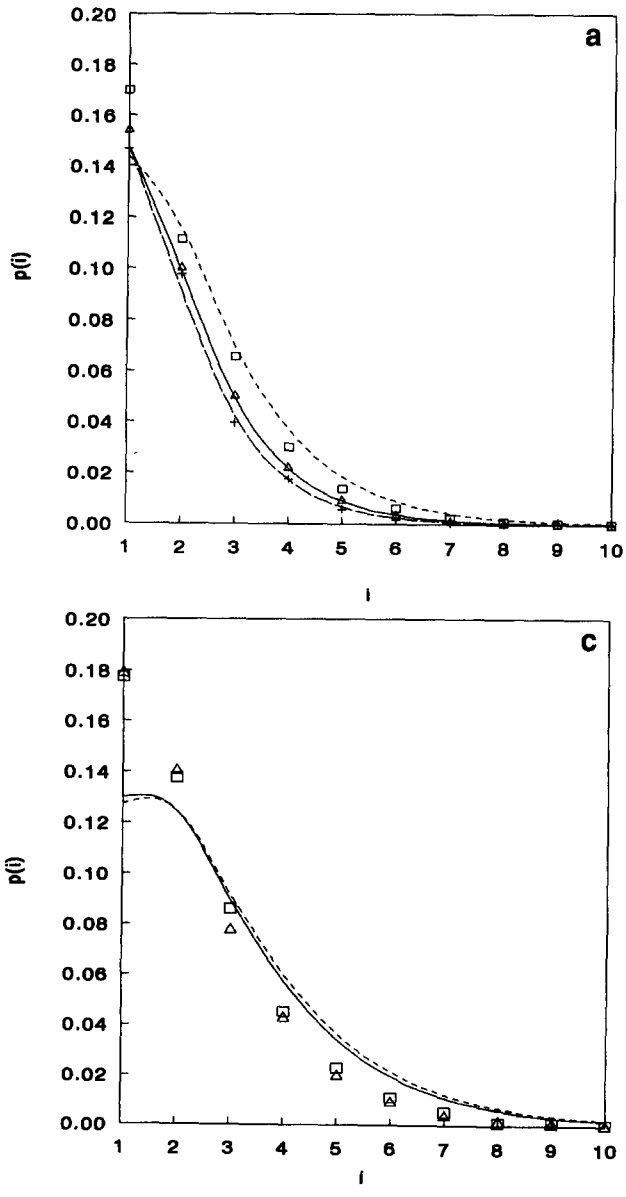

Figure 5 The fraction $p(i)$ of the all-*trans* segments of length *i*-bonds found from MC simulations with chain lengths of 100 segments. (a) Using model A(0) with relative intersegmental energy $\varepsilon_s = 2.0$ (□), -0.4634 (△) and -1.0 (+). The lines represent the prediction of the sequence distribution by equation (1): – – –, ——, and ——— correspond to $\varepsilon_s = 2.0$, 0.4634 and -1.0, respectively. (b) Using model A(1) with relative intersegmental energy $\varepsilon_s = 2.0$ (□), 0.0 (△) and -1.0 (+). The lines represent the prediction of the sequence distribution by equation (1): – – –, ——, and ——— correspond to $\varepsilon_s = 2.0$, 0.0 and -1.0, respectively. (c) Using model B(0) with relative intersegmental energy $\varepsilon_s = 1.0$ (□) and -0.8 (△). The lines represent the prediction of the sequence distribution by equation (1): – – – and —— correspond to $\varepsilon_s = 1.0$ and -0.8, respectively

The MC data for the sequence statistics are compared in *Figures 5a–c* with the results based on the probability treatment of sequences of independent bonds. The probability of a sequence of i-bonds in the *trans* state is proportional to $(1-x_g)^i$. The probability of the occurrence of a *trans* bond in the above sequence is $i(1-x_g)^i$. Then the fraction of the *trans* bonds in a given sequence (from the overall *trans* bonds in a chain) is:

$$p(i)=(1-x_g)i(1-x_g)^i/\sum_i i(1-x_g)^i \qquad (1)$$

The summation of all fractions $p(i)$ up to infinitely long all-*trans* sequences provides the overall population of the *trans* state $(1-x_g)$.

The distribution of sequences computed according to equation (1) is compared in *Figures 5a–c* with the MC results by using the x_g values appropriate for each model and the parameter ε_s. A favourable agreement, especially for the theta state, is observed between the MC results and equation (1) for model A (*Figures 5a* and *b*). It should be pointed out that equation (1) is derived for a chain with independent conformational states, neglecting the coupling of bonds such as in the pentane effect; model A involves the same assumptions but for self-avoiding chains. *Figure 5c* shows, however, that equation (1) cannot justifiably be used for the prediction of the sequence statistics in the chains where the pentane effect, as well as the 'hard-core' treatment of EV interaction, applies, i.e. model B.

DISCUSSION

The MC simulations show that the extent of the solvent-induced rotational isomerization in a chain is markedly affected by the methods of incorporation of local interactions and the EV effect in the calculations. By neglecting the chain thickness and the pentane effect, the population of the *gauche* conformations x_g in the macromolecular backbone changes by several per cent in short and flexible chains (*Table 1*). In contrast, the population x_g remains almost constant by the coil expansion in the longer, semiflexible chains and the explicit considerations of the chain thickness and of the pentane effect.

The average population of the individual conformers in a chain is a quantity which, to date, has seldom been evaluated in conformational statistics. In principle, this type of information is also accessible from measurements by various spectroscopic methods. The conformer populations are influenced primarily by temperature and the phase state of polymer materials. The phase transitions such as melting are usually accompanied by dramatic changes in the conformer populations. External force-fields, such as pressure[13], presence of pore walls[14], mechanical force[15] etc. affect the conformational equilibrium in chains to a much lesser degree. The present calculations suggest that the quality of solvent also belongs to the latter category of factors of secondary importance.

The inclusion of EV interactions according to model A is a common procedure used in theoretical studies of various properties of chains on a lattice[7,11]. Model A applied to an athermal system ($\varepsilon_s=0$) of highly flexible coils ($\varepsilon_g=0$) gives the fraction of the *gauche* states x_g (*Figures 3* and *4*), which approaches the 'ideal' value of 2/3 with an identical probability for each of the three conformational states of a bond. As already observed for an athermal system[7], an increase in the chain stiffness to $\varepsilon_g=1$ considerably reduces x_g to a value of about 0.45. The value $\varepsilon_g=1$ imitates approximately the stiffness of the polymethylene chain for which x_g is about 0.4 (ref. 1). However, the neglect of the pentane effect (assuming $\omega=1$) represents a serious handicap in model A. The mutual interdependence of the torsional potentials of two adjacent bonds in chains requires the choice of parameter $\omega \ll 1$. In addition, EV interactions are treated in model A by the 'soft' self-avoiding requirement only. Regardless of those reservations, model A may be well suited for investigations of the overall chain properties such as the scaling relations.

In model B, the treatment of local interactions is ameliorated by a realistic choice of the parameter ω. However, a proper partition of non-local interactions in model B is a matter of discussion. In the usual concept, based on the RIS theory[1], all non-local interactions are neglected and the unperturbed dimensions are based on local interactions only. Consequently, all non-local interactions contribute to the EV effect. This reasoning, combined with an assumption of the hard-core repulsion between the C...C contacts, was used[8,9,16] in the calculations of the EV effect and of the expansion coefficient α for long-chain paraffins and polymethylene.

The alternative concept[10,11], to partition non-local interactions, is based on the argument that at the theta state there exist conformations with short-range correlations between the groups separated by several (10–15) bonds such as in the 'undecane effect'[11]. In addition, in spite of the compensation of attractive and repulsive interactions within a chain and with solvent at the theta state, an inherent volume of a group inaccessible to a neighbour contact group (covolume) is always present. According to this concept[10,11], the RIS model underestimates the unperturbed dimensions because both contributions of non-local interactions are neglected by the RIS model. The analysis of interactions and dimensions of chains generated by the MC method on different lattices at the theta condition predicts that in hydrocarbon polymers the contribution of non-local interactions may augment the RIS-based unperturbed dimension by about 20%, depending on chain length.

The above-mentioned part of non-local interactions is not identified in model B and instead their complete sum is used. Thus, from the standpoint of the alternative approach[10,11] the calculation of the expansion coefficient α in model B should slightly overestimate the EV effect. It should be noted in this context that for off-lattice chains Mattice[2–4] assigned (empirically) the EV effect to interactions of groups separated by more than six or eight bonds. Overall, it seems that both models A and B represent notional extremes in a treatment of the EV effect in lattice calculations. The corresponding changes of the conformer populations due to coil swelling in real long-chain polymers should be within the limits set by both models and probably fairly close to the predictions of model B. Rigby and Stepto[9] also considered off-lattice chains and showed that there was not a one-to-one relationship with lattice chains. They also showed that the effective EV interaction per segment depended on the number of bonds between an interacting pair, due to the restrictions on the relative position of the pair because they are chemically connected.

The scarce data in literature on the influence of

EV interaction on conformer equilibrium seem to favour the predictions based on model B. For example, it is a common (and tacit) assumption in various theories of polymer properties, such as the Flory–Huggins theory of polymer solutions, that the conformer populations are independent of solvent quality (or polymer concentration). More direct support for the results based on model B comes from the RIS calculations[15] of the conformer isomerization due to the elastic stretching of coils. The calculations[15] for polyethylene and vinyl polymers showed that the minor changes in the conformer populations suffice to produce the large elongation of coils. For example in polyethylene, an increase of the square of the elongation λ^2 from unity to two reduces the number of *gauche* bonds in a long macromolecule by 0.76 bonds. In other words, the *gauche–trans* isomerization of one bond only, provides considerable alterations in the chain dimensions. Since the expansion of coils by a mechanical force and by EV interaction are related processes, the sensitivity of coefficients λ and α to the population x_g should be similar. From the slopes $\gamma^* = dx_g/d\alpha^2$ listed in *Table 1*, model B(1) provides a figure close to that cited above: the 'unperturbed' population x_g of about 0.35 in the vicinity of the theta state diminishes by 8×10^{-3} to a 'perturbed' value in a good solvent for which the expansion coefficient is $\alpha^2 = 2$. For example, in a chain 100 bonds in length with 35 *gauche* bonds, 0.8 bonds should isomerize from the *gauche* to the *trans* states due to chain swelling from unperturbed dimensions to $\alpha = 1.414$.

The assumption of the negligible effect of EV on the population x_g was crucial in the extension[5] of the RIS matrix method to chains perturbed by long-range EV interactions. According to this treatment[5] the coil expansion in good solvents should affect the higher-order probabilities of the bond states only: the influence of long-range interactions should diminish as one considers probabilities of successively lower order and it should become negligible for probability of the first order. The authors[5] reported the marked effect of solvent on the probability of pairs, triads and longer sequences of the all-*trans* bonds. Our results, shown in *Figure 5*, do not support such a treatment of EV interactions by the RIS matrix method. Within computational error, the relative sensitivity of the first-order and higher-order probabilities to the solvent quality is roughly comparable. Accordingly, there seems to be no reason for the neglect of this effect specifically in the case of the first-order probabilities x_t or x_g.

CONCLUSIONS

We have found that the variation of the fraction of *gauche* conformers x_g in the chain backbone with the solvent quality is decisively affected by the manner in which excluded volume interactions are incorporated in lattice simulations. For short molecules and reduced chain 'thickness' the fraction x_g may change by about 10% at the transition from the collapsed to the expanded coil. On the other hand, in the similar transition in the long chains with moderate chain 'thickness' the calculations predict a change in x_g of less than 1%. To a lesser degree, the above changes in the fraction x_g are influenced by variations in macromolecular flexibility. The results of the statistics of all-*trans* sequences suggest that coil expansion in good solvents is accompanied by modification of the x_g (or x_t) fractions and the populations of the longer sequences.

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