Simulating Θ-Conditions in Polymers by Modifying the Long-Range Interactions: A Monte Carlo Approach to Polymethylene

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ABSTRACT: Monte Carlo simulations on a single polymethylene chain using a *scaled* Lennard-Jones (LJ) potential of the form

$$U(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \beta\left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

and a *continuous* rotational potential (opposite to RIS models) are reported. In this approach a single parameter β models solvent quality. By adjusting the scaling parameter β to 0.55 it was shown that Θ-conditions can be simulated. In a second approach the unscaled LJ potential was taken into account up to a specified number of nearest neighbors only (*truncated* LJ potential). Regarding Θ-conditions, very good agreement was observed between the dimensions of the polymethylene chains as obtained from the model using the scaled LJ potential and the model involving the truncated LJ potential with terms retained up to the 1,6-interactions. Smaller differences in the shape of the coils as corroborated from a detailed analysis of the data were found as expected. From these results it is conjectured that simulations with complete neglect of long-range interaction but taking appropriately chosen short-range forces into account can lead to a good description of the dimensions of polymer chains under Θ-conditions. This method is by far computationally less demanding than when accounting for the LJ potential over all atom pairs.

Introduction

Computer modeling of polymers has a long tradition. The majority of simulations are based on lattice models or on simplified continuum models.[1-4] Alternatively, the modeling of molecular systems with real chemical structure in which molecules are considered from an atomistic point of view is a well-established technique in different fields of chemistry.[5-7] In the last few years there is an increasing interest to apply these molecular modeling techniques to polymeric systems.[8] The aim for the future is to calculate and predict the macroscopic properties of polymers from its microscopic properties and finally to be able to design new polymer materials with new or improved properties. When modeling synthetic macromolecules one has to realize that a very large number of possible conformations make an essential contribution to the equilibrium properties. For scanning the conformational space one could either employ molecular dynamics (MD) or Monte Carlo (MC) techniques. At present realistic overall run times allow but for a small region of accessible phase space in MD simulations. Alternatively, MC methods are a powerful tool for effectively probing conformational space and for selecting the relevant states according to their probability distribution.

In order to allow for a comparison between simulated and experimental data it is important that both are related to the same reference situation. In the case of polymeric chains the most prominent one is the so-called Θ-state.[9] Speaking more generally first, there exist two equivalent definitions of the Θ-state. Flory[10,11] defined the Θ-state by relating the radius of gyration $\langle s^2 \rangle$ and end-to-end distance $\langle r^2 \rangle$ of a chain to the values $\langle s^2 \rangle_0$ and $\langle r^2 \rangle_0$ of the equivalent ideal, i.e., self-intersecting, chain with the same

short-range interactions but without long-range interactions:

$$\langle s^2 \rangle = \alpha_s^2 \langle s^2 \rangle_0 \tag{1.1}$$

$$\langle r^2 \rangle = \alpha_r^2 \langle r^2 \rangle_0 \tag{1.2}$$

α_s and α_r are called linear expansion factors.[9,11] The other definition is based on scaling laws:[12]

$$\langle s^2 \rangle = k_1 n^\delta \tag{2.1}$$

$$\langle r^2 \rangle = k_2 n^\delta \tag{2.2}$$

where n is the number of bonds in the polymer chain ($n \gg 1$) and δ is an exponent depending on solvent quality[12] ($0.67 < \delta < 1.2$; $\delta = 1.2$ for a good solvent, $\delta = 0.67$ for a bad solvent, and $\delta = 1$ when the system is under Θ-conditions). In principle the parameter α is n-dependent, i.e., $\alpha = \alpha(n)$. (We have used Flory's notation[10] throughout.) The coefficients k_1 and k_2 reflect the short-range interactions. A variety of experimental investigations have been performed to measure properties like $\langle s^2 \rangle$ or related ones (see, e.g., refs 10 and 13). When returning to the Θ-state, this state is characterized by the condition that the effects of the attractive and repulsive parts of the long-range interactions cancel each other. This implies $\alpha_s, \alpha_r = 1$ and $\delta = 1$. From a thermodynamic point of view this means that the second virial coefficient vanishes at the Θ-point.

In a *good* solvent, generally defined by $\alpha^2 > 1$, the polymer chain swells and forms a large coil. A *bad* solvent means that a monomer unit prefers to be in contact with another monomer unit of the same or a neighboring chain. As a matter of course the macromolecular coil shrinks and

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tends to build a dense globule. Under Θ-conditions ($\alpha^2 = 1$) the solvents is just *bad* enough to compensate the chain expansion caused by excluded volume.

When adopting a standard Lennard-Jones potential to describe the medium- and long-range interactions in a single macromolecular chain, the conformation will converge toward a compact globule. It is the aim of this paper to demonstrate that conformational statistics of a macromolecular chain under Θ-*conditions* can be obtained by *modifying* the long-range inter- and intrachain interactions. The importance of simulating Θ-conditions is greatly enhanced when recognizing that polymer chains in a polymer melt and bulk amorphous polymers also adopt a scaling law $\langle s^2 \rangle \propto n$ and $\langle r^2 \rangle \propto n$. The proportionality coefficients k_1 and k_2 (see eqs 1 and 2) are usually slightly different between Θ-solvent and bulk, but this is often found for different Θ-solvents as well, indicating that there are but slight differences in the short-range interactions. The ideas of Flory[14] on the similarities between the chain behavior in Θ-solvent and bulk have been confirmed in a series of experiments,[15–17] those involving neutron scattering data on deuterated single chains in a matrix of the same though nondeuterated polymer[17] being of particular importance.

In the present paper we will concentrate on the most simple polymer, i.e., polyethylene, as a model to test and illustrate our approach. In order to be compatible with Flory's notation, viz., eqs 1 and 2, and identifying the number of links (bonds) with the number of structural (monomer) units, we will talk about poly*methylene* rather than poly*ethylene*. It is noteworthy at this point to mention that a similar investigation for polymethylene has been reported by Rigby and Stepto.[18] They employed a scaled Sutherland potential of the form

$$E(r) = \infty \quad\quad r < r_c$$

$$E(r) = cr^{-6} \quad\quad r \geq r_c \quad\quad\quad (3)$$

where r_c is a suitable constant, and solvent quality is described by the parameter c. A three-step rotational isomeric state (RIS) model (t, g^+, g^-) was taken to describe the dihedral potential around the (united atom) CH_2 groups. Characteristic ratios were studied as a function of temperature and chain length. Θ-Conditions are satisfied when the chain is in the unperturbed state. To actually determine the Θ-point the moments $\langle r^q \rangle$ were compared to their unperturbed values $\langle r^q \rangle_0$. Rigby and Stepto obtained the result that the Θ-temperature thus determined was found to depend on the choice of the moments $\langle r^q \rangle$ considered. The range of the Θ-temperature was relatively small (10–20 K), though, and it was doubted whether this would be experimentally verifiable. Rigby and Stepto also considered the unscreened Lennard-Jones (LJ) potential and made the remark that "the advantage gained in the context of polymer solutions are hard to see. One cannot easily keep the repulsive core constant and systematically vary the attractive potential."

Our approach is basically different from that followed by Rigby and Stepto because we have employed a *continuous* rotational potential rather than a three-step RIS model, and we have chosen to use a standard LJ potential for the following reasons. The functional form of the LJ potential itself is definitely more realistic than that of the Sutherland potential, the latter having a *hard core* repulsive term. It was mentioned in the review by Kushick and Berne[19] (original work by Weeks et al.[20]) that from a molecular dynamics study on simple Lennard-

Jones fluids it was found that at sufficiently high densities extremely close agreement with respect to the static properties of the system was observed when comparing the results obtained on basis of the standard LJ potential and its pure repulsive part. Fisher and Hiley[21] found a connection between the magnitude of the short-range interaction and the Θ-point in lattice model calculations. *These observations support our view that the choice of a correct short-range form of the potential is physically important.* In addition to the simulations taking into account Lennard-Jones interactions between all monomers, we have also carried out simulations using a "truncated" LJ potential, where only the Lennard-Jones interactions between several next neighbors were retained.

In the next section we describe the model and the computational method. In the subsequent section we present the results on determining the value for β that corresponds to Θ-conditions and compare them with results obtained with nonscreened potentials. We discuss the Θ-state obtained by our procedure and compare it with a random walk. For this reason we have made computations for the same model without long-range interaction (i.e., the chain was allowed to intersect itself) but with different short-range interactions.

Chain Model and Monte Carlo Method

Our calculations are based on a Lennard-Jones potential with modified long-range interaction ($|i - j| > 3$)

$$U(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \beta\left(\frac{\sigma}{r_{ij}}\right)^6\right] \quad\quad (4)$$

The London dispersion term is multipled by a factor β ($0 \leq \beta \leq 1$), which describes solvent quality. As compared to, e.g., the Sutherland potential,[18] it has the advantage that it is a continuous function of r and can consequently also be used in the standard MD simulations as employed in the molecular modeling field.

In this work we have modeled the polymethylene chain as the sequence of united atoms (CH_2 and CH_3 groups are considered as one center) with fixed bond length $l = 1.54$ Å and a fixed valence angle of 109.7°. We used the dihedral potential function of Ryckaert et al.,[22,23] which was tested extensively for liquid butane and decane

$$V(\Phi) = \sum_{i=0}^{5} C_i(\cos \Phi)^i \quad\quad (5)$$

with the potential parameters $C_0 = 9.279$, $C_1 = 12.16$, $C_2 = -13.12$, $C_3 = 3.06$, $C_4 = -26.24$, and $C_5 = -31.50$ (all values in kJ/mol). With the trans-configuration at the origin of the Φ scale, the trans–gauche barrier energy at $\Phi = 60°$ equals 12.35 kJ/mol, and the energy of the gauche minimum is 2.93 kJ/mol and lies at $\Phi = 120°$.[24] The actual form of this potential is plotted in Figure 1. The Lennard-Jones interaction between all united atom pairs (i,j) for which $j > i + 3$ was chosen for all groups as eq 4 for $r_{ij} < 10$ Å, whereas $V(r_{ij}) = 0$ for $r_{ij} \geq 10$ Å, and with the L-J parameters $\epsilon = 0.4301$ kJ/mol and $\sigma = 0.374$ nm as used by van der Ploeg and Berendsen.[24] Our quest for Θ-conditions involved the variation of the value for β; i.e., we studied $\beta = 0, 0.25, 0.5, 0.55, 0.75$, and 1.0.

The Monte Carlo method involving the classical Metropolis algorithm[25] was used for all simulations. All simulations have been performed at $T = 400$ K because this temperature is very close to the range where experimentally Θ-conditions were found in Θ-solvents for polyethylene (see Flory[10] Chapter II, Table 2). For generating new states we used a pivot-algorithm[2,26] guar-
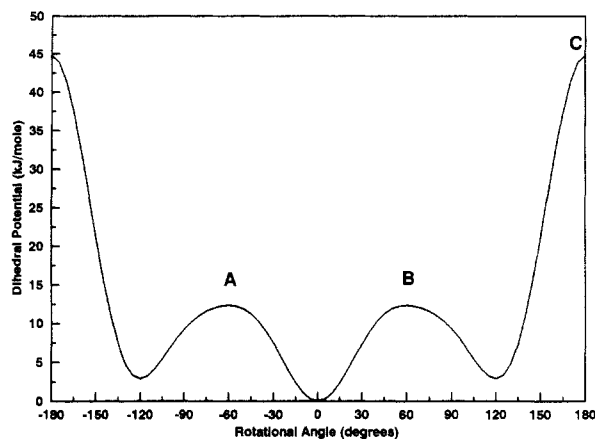
Figure 1. Dihedral potential as used in Monte Carlo simulations and as obtained from Ryckaert et al.[22,23] The intervals A–B and B–C indicate over which region in dihedral space a summation with Boltzmann weighting factors was carried out in order to calculate the statistical weight factors (for further explanation see text).

anteeing effective jumping through the conformational space of the macromolecule; i.e., for every Monte Carlo trial a random so-called pivot point (in our case a C–C bond) was chosen and then a rotation of one part of the chain around the random angle ϕ was performed.

For initial thermalization we started the calculations from some initial configurations and made 50 000 trial without averaging to obtain a starting configuration representative of given conditions. After thermalization one calculation was performed involving at least 250 000 trials for $N = 50$ and $N = 100$ and 150 000 trials for $N = 150$, N being the total number of methylene units in the chain; i.e., $N = n = 1$. For obtaining better statistics we carried out the calculations at least three times independently for each N and β (each time using a different sequence of random numbers), compared the results, and averaged. The quality of the statistics was controlled by checking the deviations between independent calculations. If not, additional independent calculations were performed. It was observed that more additional runs were required for larger N and β (up to 20 trials for $N = 150$, $\beta = 1$). One independent calculation (250 000 trials for $N = 100$ or 150 000 trials for $N = 150$) took about 2500 s on the IBM 3090 of the Rechenzentrum of the TH Darmstadt. The percentage of accepted movements (success quote) was approximately 25–30% for $\beta = 0.25$ and $\beta = 0.5$, 14% for $\beta = 0.75$, and ca. 5% for $\beta = 1.0$. This quote of successful movements was essentially independent of the value of N.

For the calculations carried out with the interdependent RIS model, we have employed the RIS module that is part of Biosym's Polymer Consortium Software version 4.0.[27]

Results and Discussion

In Figure 2 the calculated values for the characteristic ratio C_n

$$C_n = \langle r^2 \rangle / n l^2 \qquad (6)$$

and its analogue for $\langle s^2 \rangle$ are plotted for our polymethylene chain as a function of the number of monomers N. The results from $\langle r^2 \rangle$ and $\langle s^2 \rangle$ are qualitatively similar, so we only discuss the results from $\langle r^2 \rangle$, i.e., C_n, explicitly. For $\beta = 0$ and $\beta = 0.25$ one observes the typical behavior of *good* solvents, whereas $\beta = 0.75$ and $\beta = 1$ reflect *bad* solvents. Θ-Conditions ($\langle r^2 \rangle \propto n$, $\langle s^2 \rangle \propto n$ for large n) are found in the vicinity of $\beta = 0.55$. These data show that modification of the dispersive part of the LJ potential enables simulation of Θ-conditions on single polymer chains.
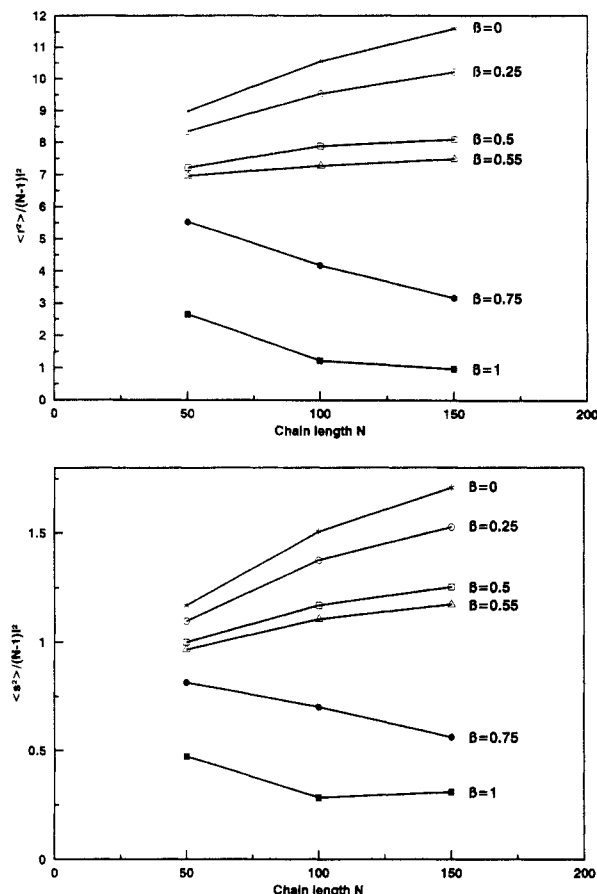

Figure 2. (a, Top) Mean square end-to-end distance $\langle r^2 \rangle$ and (b, bottom) mean square radius of gyration $\langle s^2 \rangle$, each of these being divided by $n l^2$ and plotted as a function of the number of monomers N and for different values of the scaling parameter β (eq 4).

Statistically significant values relating to the stiffness of the chain, usually expressed in the form of the persistence length, can only be obtained when the simulated chain contains at least a few of these lengths. Our result for the persistence length,[10] defined as $a = l(C_{150} + 1)/2$, is 6.5 Å. Taking this value and recognizing the possible occurrence of gauche defects, a first estimate leads to 10–15 methylene units in a persistence length. Our longest chain has 150 methylene units, which therefore meets the required criterion with respect to reliable numerical values.

The criterion that should be satisfied for having Θ-conditions is that C_n becomes a constant for large n. In the chain length domain in which we carried out our MC calculations (n up to 149), C_n still depends on n (see Figure 3). This complicates the determination of the value of the scaling parameter β in the potential eq 4 for which Θ-conditions are simulated. We have circumvented this problem by calculating the ratio between our MC C_n data and data from calculations using the interdependent RIS model. This ratio should be independent of n when simulating Θ-conditions. Turning to the RIS calculations we carried out, we first focus on one of the ingredients in the RIS model, which we did not treat in the standard way. The ingredients are the statistical weight factors for a bond pair as defined by

$$\mu_{jk} = A_{jk} \exp(-E_{jk}/RT) \qquad (7)$$

where j represents the rotational state of the first bond and k the rotational state of the second bond in the bond pair jk. The E_{jk} are energy differences between the lowest energy *trans* conformation and either one of the gauche
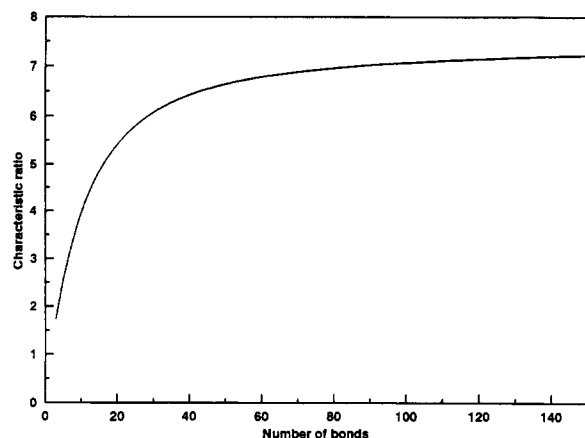
Figure 3. Calculated values for C_n from the interdependent RIS model employing the same parameters as used in our MC simulations: i.e., $E = 0.7$ kcal/mol, $T = 400$ K, a value for the valence angle of 109.5°, and our estimated values $A_{trans} = 1.0$ and $A_{gauche} = 0.87$ (the latter two are obviously implicit in the potentials used in the MC calculations).

conformations. The A_{jk} are dimensionless prefactors in which the form of the rotational energy profile can be regarded implicit. In the standard version of the interdependent RIS model, the A_{jk} are taken equal; i.e., they can be taken as unity for convenience since the E_{jk} are still adaptable parameters. In that case there are two states, i.e., the trans ground state t and the "excited" gauche state g (either g^- or g^+). It is evident that a better procedure would be to take into account the entire continuous rotational potential. In fact this potential was incorporated in the present MC calculations. In order to allow for a comparison between the form of the RIS model discussed above and our MC results, the following procedure was adopted. We accounted for the form of the rotational energy profile by taking the explicit form of the profile as we employed it in the MC calculations (for reference to the form of the potential and the marks employed in the following see Figure 1) and summing up the Boltzmann factors in the ranges A–B and B–C in 5-deg intervals. The ratio of the two resulting numbers is a first-order estimate for the ratio of the corresponding A_{jk} (note that for the BC region the local energy minimum in that range was taken as a reference for that interval). For a bond length $l = 1.54$ Å and a temperature $T = 400$ K (the same values as in the MC calculations), adopting the standard value $A_{trans} = 1$ we obtained $A_{gauche} = 0.87$.

We realize that a better estimate could be obtained when the mentioned ratio had been determined on basis of a two-dimensional plot explicitly showing the interdependences of the torsional potentials. A first-order estimate, however, *only* decreased the ratio of the A's from 1 to 0.87, whereas we will see that other factors have a much more severe impact on the numerical value calculated for the characteristic ratio C_∞.

RIS calculations were carried out employing various sets of numerical parameters. The standard parameter set in the Biosym module is $E = 0.5$ kcal/mol, $A_{jk} = 1$, and a valence angle of 112°. The Ryckaert potential we have employed has $E = 0.7$ kcal/mol, and we have also adopted a valence angle of 109.5°. In addition we can adapt the ratio of the two A values of 0.87, as this was our first-order estimated accounting for the form of the rotational potential. We combined these numerical values in different ways, thus obtaining values for C_n for these various cases as listed in Table I, with $N = 50$, 100, and 150 as in our MC calculations. Figure 3 shows the result obtained on basis of the same parameters as employed in our MC
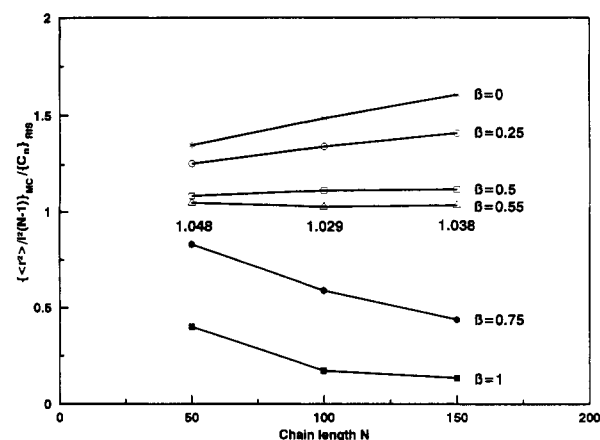

Figure 4. Square of the linear expansion coefficient α^2 calculated as $\{\langle r^2 \rangle / nl^2\}_{MC}/\{C_n\}_{RIS}$. For further explanation see text.

Table I
Calculated Values for C_N for $N = 50$, 100, and 150 at $T = 400$ K, for Different Sets of the Statistical Weights A_{jk}, the Valence Angle Φ, and the Energy Difference E between the Trans and the Gauche States

	$A_{tr} = A_g = 1$	$A_{tr} = A_g = 1$	$A_{tr} = A_g = 1$	$A_{tr} = 1$, $A_g = 0.87$
Φ	112°	109.5°	109.5°	109.5°
E, kcal/mol	0.5	0.5	0.7	0.7
C_{50}	6.23	5.68	6.23	6.64
C_{100}	6.60	6.00	6.60	7.07
C_{150}	6.73	6.11	6.73	7.21

calculations and using the estimate for the ratio between the A_{jk}; i.e., $A_{trans} = 1$ and $A_{gauche} = 0.87$.

Let us first discuss the sensitivity of C_n on the different parameters. It is corroborated from Table I that when comparing the results in columns 1 and 3, where only the value of the valence angle has been varied, a significant change in C_n is observed. An increase of the trans–gauche energy difference from 0.5 up to 0.7 kcal/mol with simultaneous decrease of the valence angle by a few degrees (columns 1 and 2) leads to a cancellation of effects, i.e., identical C_n values. Table I also contains the data indicating the effect of the precise choice for the statistical weight factors A_{jk}. It is the purpose of the present paper to focus on the scaling behavior rather than explaining the differences between calculated and experimental C_n values in detail, and we suffice to emphasize the sensitivity of the calculated values on the input parameter values.

The next step is to calculate α^2 as the ratio of the data displayed in Figure 2 and the RIS data, i.e., explicitly $\{\langle r^2 \rangle / nl^2\}_{MC}/\{C_n\}_{RIS}$. The results are depicted in Figure 4. Within the limits of the accuracy of the data, we conclude that $\beta = 0.55$ corresponds to Θ-conditions. The actual value for the entity $\{\langle r^2 \rangle / nl^2\}_{MC}/\{C_n\}_{RIS}$ for $\beta = 0.55$ is around 1.04; from this one deduces that the MC calculated C_n values match extremely well with those obtained from the interdependent RIS mode. The agreement nevertheless is still very much dependent on the exact choice of the parameter values (see discussion in the above and Table I).[1]

(Moreover, in a recent paper Mattice[28] has shown that second- and third-order interactions together account for a decrease in the value of C_n of about 9%, which brings our value of 7.48 down to 6.8. The physical basis of these effects are small correlations between torsions that lead to small changes of typically 5° in some torsional angles. Energy minimization performed on hexane using our united atom approach showed that these second- and third-order interactions are not accounted for by a united-atom
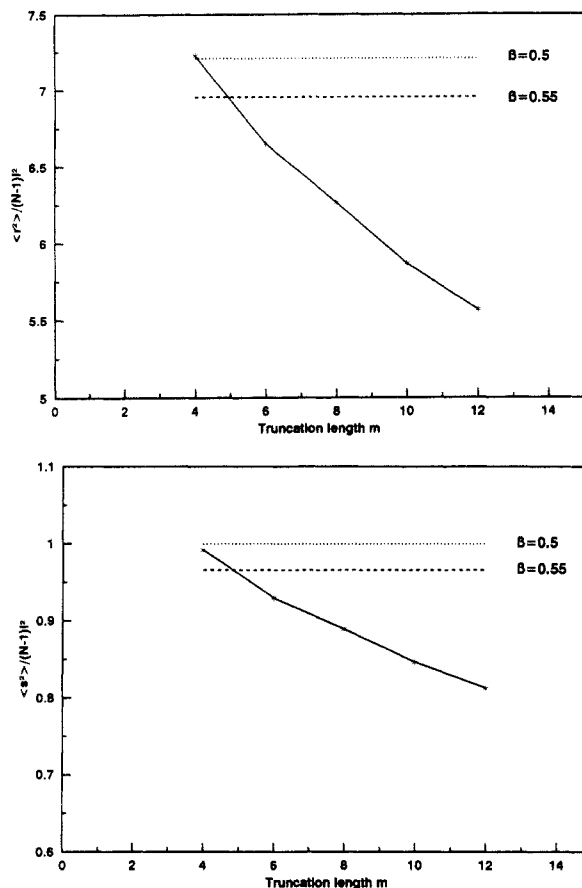
Figure 5. (a, Top) $\langle r^2 \rangle / nl^2$ and (b, bottom) $\langle s^2 \rangle / nl^2$ for the self-intersecting chain (truncated LJ potential) and plotted as a function of the truncation length m (starting with the 1,5 interactions retained only). $m = 2$ would thus correspond to retaining the valence potential only; $m = 3$ also retains the dihedral potential, whereas $m = 4$ (retaining up to the fourth neighbor) includes up to the first LJ interaction, i.e., the 1,5 interaction. The dashed line indicates the value of $\langle r^2 \rangle$ that corresponds to Θ-conditions as corroborted from the calculations employing the scaled LJ potential, eq 4, i.e., $\beta = 0.55$. The dotted line corresponds to $\beta = 0.5$ in the scaled LJ potential. The number of monomer units in a chain is $N = 50$.

force field. An all-atom force field calculation on hexane did reveal the effects reported by Mattice, however. We see again that the calculated result depends very much on the choice of the parameter values employed. We emphasize that in the present work we aim to demonstrate the feasibility of the method we propose, rather than to get the most accurate numbers.)

In order to gain more insight about Θ-conditions obtained from modified LJ potentials, we have calculated the mean square radii of gyration and the mean square end-to-end distance on basis of a truncated LJ potential

$$U_{\text{total}} = 4\epsilon \sum_{3 \le |i-j| \le m} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \qquad (8)$$

m being the truncation length in the truncated potential as defined by the maximum number of neighboring CH_2 groups on each side that are incorported (truncation is along the chain only). Since now only short-range interactions are taken into account, the chain can be self-intersecting and adopts unperturbed dimensions. The results have been displayed in Figure 5 for $N = 50$ and in Figure 6 for $N = 150$. It might be noted that the qualitative change in behavior of the curves drawn in these figures is closely related due to the fact that from $m = 5$ up the interdependence between rotations is incorporated. Focusing on Θ-conditions ($\beta = 0.55$), it can be seen from
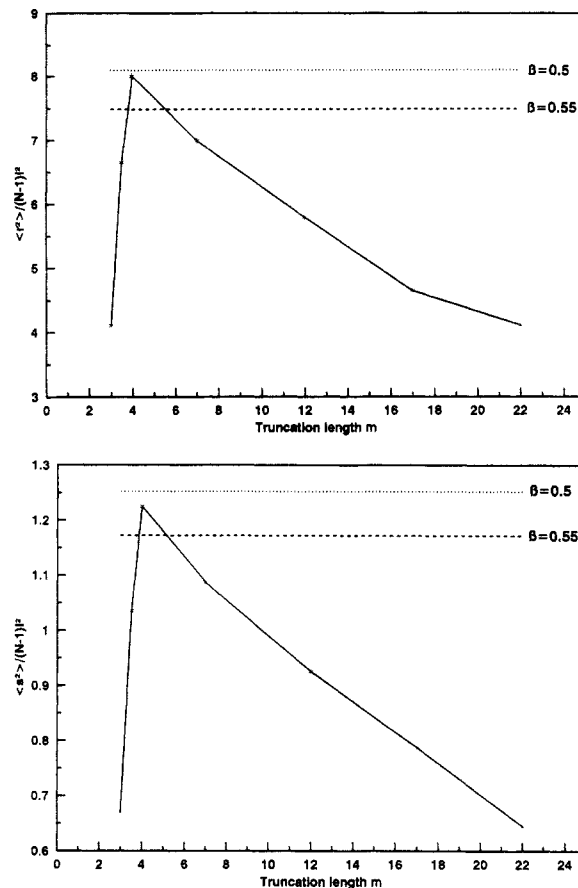

Figure 6. (a, Top) $\langle r^2 \rangle / nl^2$ and (b, bottom) $\langle s^2 \rangle / nl^2$ for the self-intersecting chain (truncated LJ potential) plotted as a function of the truncation length m (starting with the 1,5 interactions retained only). $m = 2$ would correspond to retaining the valence potential only; $m = 3$ also retains the dihedral potential, whereas $m = 4$ (retaining up to the fourth neighbor) includes up to the first LJ interaction, i.e., the 1,5 interaction. The dashed line indicates the value of $\langle r^2 \rangle$ that corresponds to Θ-conditions as corroborated from the calculations employing the scaled LJ potential, eq 4, i.e., $\beta = 0.55$. The dotted line corresponds to $\beta = 0.5$ in the scaled LJ potential. The number of monomer units in a chain is $N = 150$.

Figures 5 and 6 that the values for C_n and its analogue for $\langle s^2 \rangle$ we obtained on the *scaled* LJ potential will practically coincide with those of the *truncated* LJ potential when in the latter interactions up to $m = |i - j| = 5$ units are taken into account. It might be emphasized that all data points displayed in Figures 5 and 6 and based on the truncated LJ potential, i.e., these are self-intersecting and unperturbed chains, obey the scaling laws appropriate to Θ-conditions, but this does not imply the average chain dimensions reflected by a quantity like $\langle r^2 \rangle$ is correct. Such cases where the scaling laws are obeyed but an incorrect characteristic ratio is obtained reflect a system that does not correspond to polymethylene but to some hypothetical other polymeric system with a potential that yields another characteristic ratio under Θ-conditions.

We conclude that the statistics of a model chain with the LJ potential truncated to $m = 5$ neighbors are in good agreement with the results obtained on the same chain with a scaled LJ potential (eq 4, a contracted self-avoiding walk under Θ-conditions). In the Introduction we have referred to a similar conclusion that was obtained from MD simulations on simple LJ fluids.[19,20] It is of considerable practical importance to note then that a considerable savings in computer resources is gained in this way.

We finally focus attention on a more subtle detail of the calculations. Figure 7 shows the segment density distri-
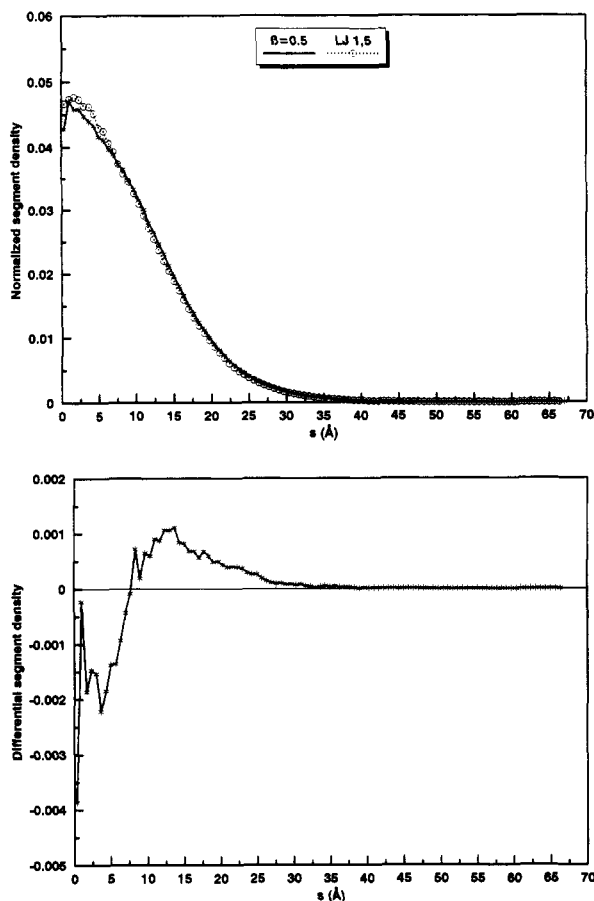
Figure 7. (a, Top) The segment (methylene monomer) density distribution as calculated on the basis of the scaled LJ potential (□), eq 4 (β = 0.5) and the truncated LJ potential with 1,5 interactions retained only (+). (b, Bottom) The differential segment density of the densities plotted in part a. The difference is plotted as the segment density of the scaled LJ minus that of the truncated LJ potential as a function of the center of mass.

bution around the center of mass for both the scaled LJ potential (β = 0.5) and the truncated (1,5 LJ interactions only) LJ potential. We have taken these two sets to compare because the sets now selected have the same average chain dimensions ($\langle r^2 \rangle$ and $\langle s^2 \rangle$) and they are close to Θ-conditions (β = 0.5 versus β = 0.55 for true Θ-conditions). This is instigated by the fact that we actually do not have available the MC results based on the truncated potential including up to 1,6-interactions. Since the model involving the truncated potential allows segments other then 1,5 to intersect, it essentially yields conformations that are unperturbed by excluded volume effects. Adaptation of the scaled LJ potential results in self-avoiding conformations. The excluded volume effect then involved will be maximum where the segment density is highest, i.e., near the center of mass of the polymer chain. It is therefore expected for the model with scaled LJ interactions to see a reduced density at small distances from the center of mass (s), as compared to the corresponding values obtained on the truncated LJ potential involving only 1,5 interactions. The presence of long-range attractive forces in the scaled LJ potential causes the segment density at intermediate distances from the center of mass to be larger for the scaled LJ potential model as compared for the model with the truncated LJ potential. This is what we see indeed by comparing the two histograms in Figure 7. In fact, Figure 7 explicitly shows that two sets of polymer chains having identical $\langle r^2 \rangle$ and $\langle s^2 \rangle$ do not necessarily have the same shape of the polymer coils.

The scaled LJ potential causes the outer parts of the coil to be tracted more toward the center as compared to the truncated LJ case. The fact that one does not observe any differences in the distributions at larger distances as they originate from the scaled and the truncated LJ potential must imply that the strength of the LJ interaction is so weak at those distances that it does not influence the chain conformation to a detectable extent.

One might have some reservations about whether such details can be corroborated from the calculations with any confidence. In this respect we point to the very good statistics concerning the data displayed in Figure 7, indicated by the very low level of scatter in the histograms.

Summary and Conclusions

The primary aim of this work was to model the Θ-state where repulsive and attractive parts of long-range interactions compensate each other. Monte Carlo simulations have been performed for polymethylene with different chain lengths at 400 K. For these systems Θ-conditions could be simulated by scaling the dispersive part of the van der Waals interactions by a factor $\beta \approx 0.55$. For this value the statistics of the macromolecule obeys the scaling laws $\langle r \rangle^2 \propto n$, $\langle s \rangle^2 \propto n$ in the limit of large n. We compared this Θ-state with the results obtained from simulations on self-intersecting chains as simulated by introducing a truncated LJ potential; i.e., only a limited number of nearest-neighboring segments were considered as interacting through a LJ potential. It was found that if we introduced the Lennard-Jones interactions between each ith and $(i + 5)$th monomers (1,6 interactions only), the same values for $\langle r^2 \rangle$ and $\langle s^2 \rangle$ result as for the effective Θ-point situation; i.e., we have again simulated Θ-conditions. Expected small differences between the two approaches (scaled and truncated LJ potential, respectively) showed up near the center of mass of the coils.

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