(7) Rippen, G.; Klöpffer, W. *Ber. Bunsenges. Phys. Chem.* 1979, *83*, 437.
(8) Burkhart, R. D.; Avilês, R. G. *Macromolecules* 1979, *12*, 1078.
(9) Burkhart, R. D.; Avilês, R. G. *J. Phys. Chem.* 1979, *83*, 1897.
(10) Abia, A. A.; Burkhart, R. D. *Macromolecules* 1984, *17*, 2739 and earlier references cited therein.
(11) Burkhart, R. D.; Howells, P. N. *J. Chem. Educ.* 1979, *56*, 249.
(12) Johnson, G. E. *J. Chem. Phys.* 1975, *62*, 4697.
(13) Vala, M. T.,; Haebig, J.; Rice, S. A. *J. Chem. Phys.* 1965, *43*, 886.
(14) Burkhart, R. D.; Avilês, R. G.; Magrini, K. *Macromolecules* 1981, *14*, 91.
(15) Turro, N. J.; Chow, M.-F.; Burkhart, R. D. *Chem. Phys. Lett.* 1981, *80*, 146.

Monte Carlo Calculations for Linear and Star Polymers with Intramolecular Interactions. 1. Dimensions

Juan J. Freire,* Jesús Pla, Antonio Rey, and Rosa Prats

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain. *Received January 21, 1985*

ABSTRACT: A polymer model that includes a Gaussian distribution of distances between neighboring elements and a Lennard-Jones intramolecular potential to account for long-range interactions has been applied to describe the change with temperature of the linear chain dimensions with different values of the number of chain elements, N. The calculations have been performed by means of a Monte Carlo method. The results for the low- and high-temperature ranges have been analyzed, and the reduced temperature for which the mean quadratic radii of gyration are proportional to N is adopted as the unperturbed state. Monte Carlo calculations for star chains with different numbers of arms at this reduced temperature and subsequent extrapolation to the long-chain limit have allowed us to obtain values of the dimension ratio g in fair agreement with experimental data. The influence of finite-size effects on the validity of the different features shown by the model is explicitly discussed.

Introduction

Determining the influence of temperature on the conformational properties of a polymer chain in dilute solution has been the goal of many studies in the past.[1,2] This influence affects the balance between the intramolecular interactions of polymer segments and the interactions of these segments with the solvent. At high temperatures the long-range repulsive intramolecular interactions give rise to the excluded-volume effect, and the polymer becomes a swollen coil. At low temperatures the segments try to avoid contact with the solvent and the polymer collapses, adopting a globular form. At $T = \Theta$ (theta temperature) for a given solvent, both types of interactions are equivalent and the polymer is in its unperturbed state. The polymer collapse in the low-temperature region competes with condensation of the polymer phase so that only recent experimental studies[3-5] performed at high dilution have been able to detect the transition to the globular form.

From the theoretical macroscopic point of view, the coil–globule transition can be described through extended versions of the Flory mean field theory.[1,2] These types of approaches, together with the approximation $T \approx \Theta$ (i.e., for temperatures not too different from $T = \Theta$), lead to equations with the generic form[4]

$$\alpha^5 - \alpha^3 - \gamma^2/\alpha^3 = CN^{1/2}(1 - \Theta/T) \qquad (1)$$

where α^2 is the expansion factor of the polymer mean quadratic radius of gyration ($\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_\Theta$, i.e., the ratio between the mean quadratic radii of gyration at T and Θ). C is a numerical constant, and γ is a parameter proportional to the volume of a segment. The only change of eq 1 with respect to the well-known Flory equation is the addition of term $-\gamma^2/\alpha^3$, taking care of the contribution of three-body clusters to the free energy.

A different insight is provided by numerical results obtained from simulation calculations based on polymer models. These models include intramolecular potentials with attractive and repulsive terms so that they can mimic in a first approximation the balance of intramolecular and polymer–solvent interactions. This way the solvent structure can be excluded from the simulation procedures. Thus, McCrackin et al.[6] used a lattice model for the polymer in which repulsions between the chain elements were represented by a hard-sphere potential and attractions between elements in neighboring sites were described by a parametric constant. More recently, Baumgärtner[7] has used an off-lattice polymer model composed by beads jointed by randomly oriented rigid bonds, the beads interacting through a Lennard-Jones (LJ) potential. In this model each bond is understood to represent a segment of a real chain so that each segment consists of an average number of skeletal atoms. The length of the segments does not depend on temperature and is chosen to be larger than the hard-core distance of the intramolecular forces, taking into account the limited flexibility of the real polymer. The long-range attraction between the bonds resulting from the mutual interaction of polymer and solvent is taken into account by the LJ potential, whose depth measures, at least in a first approximation, the energy of the polymer–polymer intramolecular interaction relative to that of the polymer–solvent interaction. This type of relatively soft potential seems somewhat more realistic than hard-core potentials to describe interactions between units representing flexible subchains for which the real interactions between chemical groups included in the interacting theoretical beads are not simple functions of the distance between the bead centers. Also, Webman et al.[8] have studied a model that considers beads connected by springs and interacting according with a LJ potential. The latter model seems to be more realistic since the segments of a long flexible chain can be described as Gaussian subchains and a Gaussian distribution of distances is also followed in the spring–bead model. However, the mean distance between neighboring segments, b, is in this model temperature-dependent since LJ interactions are also considered between these segments.

These off-lattice methods, in addition to being more realistic than lattice models, also offer the possibility of varying more parameters relevant to the problem (in the

0024-9297/86/2219-0452$01.50/0

case of the LJ potential both the energetic and steric parameters can be independently changed) without being restricted to lattice constraints. Their main shortcoming is that only chains with a relatively small number of units can be generated. Then, they are based on the assumption that large-scale properties of the polymer do not depend much on the precise nature of interactions and might manifest themselves already for small values of N. In fact, both the Baumgärtner and the Webman et al. works show that the power laws governing the N dependence of dimensions at high temperatures and even some characteristics of their variation with varying temperature can be obtained with small chains. The limitation of chain size, however, makes it difficult to analyze more subtle questions concerning the behavior of long chains at intermediate and low temperatures.

In the present work we describe simulations performed with a model slightly different and more realistic than that used by Webman et al.[8] We have considered a set of $N + 1$ beads joined by N flexible bonds, whose lengths are Gaussianly distributed and have taken into account intramolecular interactions through a LJ potential only for nonneighboring beads (long-range interactions). Consequently, b is independent of temperature. Our aim has been to describe the change of dimensions with temperature, reaching the globular state at low temperatures, to reproduce the experimentally shown behavior in the limit of high temperatures (or good solvent), and to investigate the ability of the model to reproduce experimental temperature expansions of real flexible polymers by using a moderate number of theoretical chain elements.

Moreover, we have also investigated the performance of the model applied to describe starlike polymers in their unperturbed state. Previous simulations on this type of polymers were restricted to lattice models.[9,10] Our interest has been focused in the magnitude g, defined as

$$g = \langle S^2\rangle_b/\langle S^2\rangle_l \tag{2}$$

i.e., the ratio of the quadratic mean radius of gyration of the star polymer, $\langle S^2\rangle_b$, to that of a linear polymer of the same molecular weight, $\langle S^2\rangle_l$. The lattice simulation yielded values of g considerably higher than those corresponding to the Gaussian statistics attributed to the unperturbed state and also slightly higher than those found experimentally for samples in Θ conditions. With the simulations described here we try to study the influence that the polymer model may have in the values for g and, moreover, check the model studied here through its performance with respect to the experimental values.

Finally, we should remark that the model employed in this work and the conclusions derived from its study have been applied to the nonpreaveraged description of the hydrodynamic properties of both linear and star polymers. The results of such an investigation are reported in a subsequent paper.[11] In this case, a lattice model would not be more helpful in the analysis of results of longer chains since the numerical solving of the hydrodynamic interaction equations severely limits the length of the chains for which such calculations are feasible.

Computational Procedures

As explained in the Introduction, we consider a model consisting of $N + 1$ beads joined by means of N bonds of Gaussianly distributed lengths. The nonneighboring beads interact through a LJ potential so that the interaction energy between two beads i and j separated by a distance r_{ij} is given by

$$U(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6] \tag{3}$$

ϵ and σ being the energetic and steric parameters of the model.

Then, the statistical weight corresponding to the total interaction energy in a given conformation is calculated as

$$w = \exp[-\sum_i\sum_j U(r_{ij}/b)/k_BT] \tag{4}$$

where the sum extends over all nonneighboring pairs of different beads i and j. Therefore, w depends on the temperature through the reduced energetic parameter ϵ/k_BT and also depends on a second reduced parameter, σ/b, which describes the ratio between the LJ diameter and the theoretical bond statistical length. Since ϵ depends on the balance between polymer–solvent and intramolecular polymer interactions, a change in ϵ/k_BT implies a change in temperature for a given polymer–solvent system or, as an alternative, a change in the solvent quality at a given temperature.

The quadratic radius of gyration of a conformation is computed as

$$S^2 = [1/(N + 1)^2]\sum_{i=1}^{N+1}\sum_{j=1}^{N+1} r_{ij}^2 \tag{5}$$

In order to generate the initial conformation of our Monte Carlo procedure we assign the $N + 1$ bead to the central unit. The other units are enumerated from the center to the end of each one of the arms in the star (or from the center to each one of the two ends in a linear chain) so that the bead in branch f separated from the central unit by n bonds is assigned as bead $i = (f - 1)(N/F) + n$. (F is the number of arms; $F = 2$ for linear chains, and the enumeration of the arms is arbitrary.) The positions of the beads are calculated from the coordinates X_i, Y_i, and Z_i of the bond vectors $\mathbf{R}_i$ pointing to unit i and applied from the preceding unit along the polymer backbone (i.e., the neighboring unit separated from the central bead by the smallest number of bonds). The coordinates X_i, Y_i, and Z_i are obtained from a computer-generated sequence of Gaussianly distributed numbers with an arithmetic mean $v = 0$ and with a root mean square deviation $d = {}^1/_3$. This way we obtain randomly oriented bond vectors whose root mean square length is unity (all distances are calculated relative to this length). According to our enumeration of units, the coordinates of unit i, x_i, y_i, and z_i are calculated from those of bond vectors as

$$x_i = X_i \qquad y_i = Y_i \qquad z_i = Z_i \tag{6a}$$

if unit i is linked to the central unit (which is taken as the origin), or

$$x_i = x_{i-1} + X_i \qquad y_i = y_{i-1} + Y_i \qquad z_i = z_{i-1} + Z_i \tag{6b}$$

otherwise.

The energy of this initial conformation is checked so that if it surpasses a certain moderate positive value the conformation is disregarded and a new independent trial is performed. This way we avoid initial conformations of high energy that would take a long time to relax in the stochastic process, used to obtain the rest of conformations of the sample.

We have employed two alternative procedures for the simulation of these stochastic processes, each one adequate for a different range of temperatures. In both procedures the transition probability from one conformation to another is obtained according to the Metropolis criterion: the new conformation is accepted if its interaction energy, U_{new}, is smaller than that of the old conformation, U_{old}. Otherwise, we choose a random number between 0 and 1,

ξ, and accept the new conformation if

$$\exp[-(U_{\text{new}} - U_{\text{old}})/k_{\text{B}}T] > \xi \tag{7}$$

If the new conformation is rejected, the old one is accepted again. This way we reach an equilibrium characterized by a Boltzmann distribution of conformations so that the averages of interest (in our case $\langle S^2 \rangle$) are simply obtained as arithmetic means over the values corresponding to all the accepted conformations.

In the first type of stochastic process (process a), useful for $T \geq \Theta$, the new conformation is obtained from the previous one by changing the coordinates of a randomly chosen bond vector, the new coordinates also obtained from the sequence of Gaussian numbers. The rest of the bond vectors in the chain remain unaltered so that the chain is changed from the bead to which the chosen bond vector applies up to the end of the star arm in which this vector is located (or to an end of the linear chain). These changes sometimes represent a very significant conformational rearrangement and, in fact, the transition may not be physically possible in one step. However, the equilibrium averages obtained from this purely theoretical stochastic process should be correct. The use of this type of sharp conformational transition allows us to reach the equilibrium in a fast way if a sufficiently high number of conformations can be accepted. This is not the case in the low-temperature range, $T < \Theta$, which requires smoother changes of the considerably more compact conformations. Then, as an alternative process in these cases (process b), we change only the position of a randomly selected bond by step, i.e., the coordinates x_i, y_i, and z_i. Since the possible components of bond vectors $\mathbf{R}_{i+1}$ and $\mathbf{R}_i$ should follow Gaussian distributions with $d = {}^1/_3$ and (before taking into account the LJ potential) they are mutually independent, the possible components of $\mathbf{R}_i^{\text{d}} = \mathbf{R}_{i+1} - \mathbf{R}_i$ should also follow another Gaussian distribution with $d = {}^2/_3$. Then, we select the coordinates X_i^{d}, Y_i^{d}, and Z_i^{d} of vector $\mathbf{R}_i^{\text{d}}$ from a Gaussian sequence of numbers with $d = {}^2/_3$. These coordinates are defined as

$$X_i^{\text{d}} = X_{i+1} - X_i \qquad Y_i^{\text{d}} = Y_{i+1} - Y_i$$
$$Z_i^{\text{d}} = Z_{i+1} - Z_i \tag{8}$$

and, together with the coordinates of vector $\mathbf{R}_i^{\text{S}} = \mathbf{R}_{i+1} + \mathbf{R}_i$ (which remains unaltered in the transformation since it joins beads $i - 1$ and $i + 1$)

$$X_i^{\text{S}} = X_{i+1} + X_i = x_{i+1} - x_{i-1}$$
$$Y_i^{\text{S}} = Y_{i+1} + Y_i = y_{i+1} - y_{i-1}$$
$$Z_i^{\text{S}} = Z_{i+1} + Z_i = z_{i+1} - z_{i-1} \tag{9}$$

allow us to compute the new coordinates X_i, Y_i, and Z_i of vector $\mathbf{R}_i$ (and those of vector $\mathbf{R}_{i+1}$) and consequently, the new coordinates x_i, y_i, and z_i of bead i. This transformation cannot be applied if bond i is at the end of an arm (or is an end of a linear chain). Then, its coordinates are changed by a random transformation of its bond vector, as in process a. Process b is able to give accurate averages in a reasonable amount of computational time since the distribution of significant conformations narrows as the temperature decreases. For $T \geq \Theta$, however, this procedure is not fast enough from the practical point of view.

Once a new conformation is generated in either process a or process b, the intramolecular distances r_{ij} differing from those of the previous conformation are calculated. By substracting the terms depending on the old distances and adding the terms corresponding to the new ones in the double sums of eq 4 and 5, we can calculate the values of U and S^2 for the new conformation.

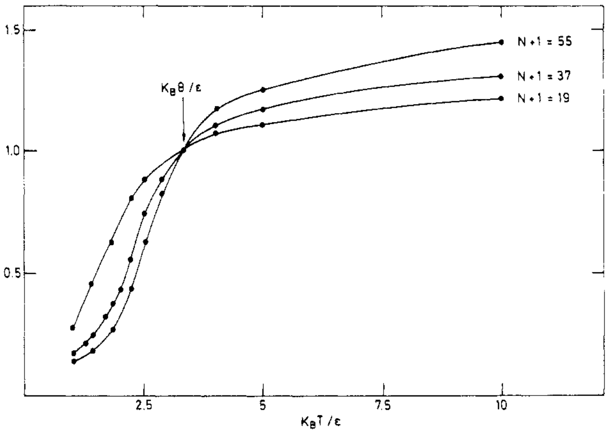

Figure 1. α^2 vs. $k_{\text{B}}T/\epsilon$ according to the results obtained for $\langle S^2 \rangle$ with $\sigma/b = 0.8$.

The sequence of Gaussian numbers defining the stochastic processes is initiated by a seed number. We use sequences from different seeds in order to obtain independently generated sets of conformations (samples) for the computation of a given average. Generally, we use eight different samples, obtaining arithmetic means and standard root means square deviations from the averages corresponding to these samples, treated as independent experimental measurements of a magnitude. The use of different samples tries to overcome (or at least to detect through deviations) the presence of metastable distributions, which are specially expected in the region of low temperatures where processes may sometimes occur in an almost nonergodic way.

Typically, we have generated 25 000 conformations per sample when using process a, and 250 000 conformations per sample with process b. The conformations generated at the initial steps of each stochastic process are disregarded so that this process can relax to its equilibrium distribution and initial effects can be eliminated.

Numerical Results and Discussion

Linear Chains. The parameters corresponding to the LJ potential are introduced in our calculations in terms of the reduced variables $\epsilon/k_{\text{B}}T$ (inversely proportional to temperature) and σ/b. In preliminary studies we have tried several values of the parameter σ/b, and we have verified that the lowest choices for this parameter were not able to reproduce a significant expansion of the model chains at high temperatures.[13] A noticeable expansion is, however, reached for the choice $\sigma/b = 0.8$, which we believe adequate to give a fair description of many aspects of the behavior of real chains. In Figure 1 we present the results corresponding to this choice for σ/b, which we will adopt hereafter. In the three curves corresponding to three different values of N, it can be observed that the plateau corresponding to the globule state is about to be reached in the low-temperature region.

For an ideal Gaussian chain the dependence of dimensions with N is

$$\langle S^2 \rangle = (Nb^2/6)[1 + 1/(N + 1)] \tag{10}$$

while, in general, we can assume the scaling law[2]

$$\langle S^2 \rangle \propto N^{2\nu} \tag{11}$$

From the numerical results of log $\langle S^2 \rangle$ and log N for chains of different numbers of bonds, we have performed a linear regression analysis in order to obtain the exponent ν. The results of this analysis are contained in Table I. For high temperatures we get $\nu = 0.60$, in accordance with previous theoretical predictions[2] and simulation results,[2,6-8]

Table I
Fitted Values of the Exponent ν for Linear Chains at Different Temperatures

ϵ/k_BT	ν	ϵ/k_BT	ν
0.10	0.60	0.45	0.22
0.20	0.57	0.55	0.12
0.25	0.55	0.70	0.08
0.30	0.50	1.00	0.22
0.40	0.35		

some of them[7,8] obtained also with a LJ potential and relatively short chains.

For $\epsilon/k_BT = 0.3$ we get the value $\nu = 0.50$, corresponding to a linear dependence of $\langle S^2\rangle$ on N so that this value of the reduced temperature reproduces the unperturbed behavior for $\sigma/b = 0.8$. Very similar values of ϵ/k_BT reproduced also the unperturbed conditions for our previous preliminary choices of σ/b.[13] Then, the parameter $\epsilon/k_BT = 0.3$ is hereafter adopted to represent Θ conditions. These conditions are defined, in fact, in a more rigorous way according to thermodynamic criterions,[2] but we prefer to adopt here the definition in terms of the variation of dimensions with N, which is directly related to our results. On the other hand, our main conclusions are not likely to be affected by small numerical differences associated to the different definitions of the Θ point, which are surely blurred by the numerical uncertainties of our results. The value of the reduced temperature corresponding to the unperturbed conditions for this model is similar to that reported by McCrackin et al.[6] and Baumgärtner[7] for their lattice and LJ chain with rigid bond models and is also close to the reduced Boyle temperature of a real gas. It should be remarked that Webman et al. found different values of ϵ/k_BT that reproduced the unperturbed state for different values of the parameter σ/b, perhaps as a consequence of using a temperature dependence definition for b.

Nevertheless, we have found that the linear relationship between $\langle S^2\rangle$ and N is of the form

$$\langle S^2\rangle = (0.225 \pm 0.002)Nb^2 \tag{12}$$

i.e., the numerical factor in front of Nb^2 is different from the $^1/_6$ coefficient expected from eq 10 for a chain without intramolecular interactions. In fact, other different numerical factors were obtained in previous simulations[6-8] with different models. Then, it can be concluded that this numerical factor defining $\langle S^2\rangle$ at the Θ point is essentially dependent on the characteristics of the chosen model.

The change of ν with temperature at $T < \Theta$ is very remarkable though, of course, it does not correspond to the discontinuity expected for the globule–coil transition of an infinitely long chain.

In the low-temperature region we get values of ν considerably smaller than that of a uniform sphere $\nu = {}^1/_3$, which would correspond to the globular state, though at still lower temperatures this exponent increases and seems to tend to that limit. Since we are dealing with chains with a small number of bonds, the spatial distribution of beads for $T < \Theta$ is strongly conditioned by steric interactions and, on the other hand, a decrease of temperature (or solvent quality) for the longest chains produces a relatively higher decrease of dimensions than that of smaller chains that are more conditioned by steric effects. These effects are clearly model-dependent and should disminish with increasing N. In fact, previous calculations with LJ models[7,8] yield similar abrupt dependences on temperature for $T < \Theta$ (see Figure 3 of ref 7 and Figure 3 of ref 8). Then, we think that a quantitative analysis of the variation of $\langle S^2\rangle$ with varying temperature with results obtained with models composed by a small number of beads is not able to yield the general behavior of a real long polymer chain. Nevertheless, the shape of the transitions for chains that are not too long as well as the dimensions of the swollen and globular form can be reproduced. In connection with the behavior of long flexible chains, the high-temperature scaling exponent can be reproduced and the model unperturbed state assigned, since the linear relationships represented by eq 11 can be obtained in the region of good or moderately poor solvents with reasonably short chains, as it can be also done in simulations on lattices.[2,6] According to these conclusions, the application of the present model to the study of star chains, which has not been previously performed with off-lattice models (next section), and the study of nonpreaveraged hydrodynamic properties, which have not been previously calculated for parametric models (following paper), can be now confidently accomplished, though the possible influence of finite size effects should be carefully analyzed in each particular case.

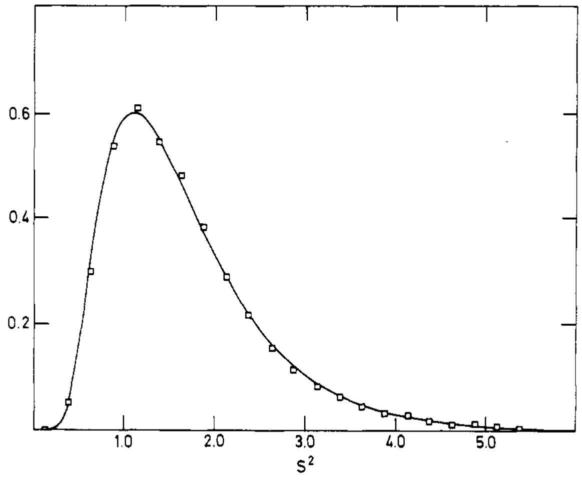

Figure 2. $W(S^2)$ vs. S^2 (S expressed in b units) for a chain of 10 elements: (—) fitting curve for the results obtained with $\epsilon/k_BT = 0.3$, $\sigma/b = 0.3$; (□) results obtained with $\epsilon/k_BT = 0$.

We have also studied the distribution function of S^2, $W(S^2)$, for the chain model used in this work, though this study has been restricted to our preliminary calculations with the parameter $\sigma/b = 0.3$. The detailed analysis of the results is given elsewhere.[13] The values of $W(S^2)$ for $N + 1 = 10$, 20, and 50 have been fitted to

$$W(S^2) = C_1S \exp[-(\pi^2S^2/4\langle S^2\rangle_\Theta) - C_2S^{-3}] \tag{13}$$

corresponding to the asymptotic expression given by Fixman for a long Gaussian chain to which we have added a perturbation term according to the Flory excluded-volume theory.[12] As this theory, eq 13 is only valid in the $T \geq \Theta$ region where we have found satisfactory fittings for all cases. As it can be expected, the distribution function narrows for decreasing temperatures. For $\epsilon/k_BT = 0.3$ we have found that C_2 does not vanish, so that the Fixman distribution is not followed at $T = \Theta$. It should be noted, however, that this function is only valid for high values of S. Then, the term C_2 is not only depending on intramolecular interactions but also accounts for deviations of the real distribution of S in Gaussian chains with respect to the form predicted by eq 13 with $C_2 = 0$. In fact, the distribution functions obtained with $T = \Theta$ are almost reproduced by generating chains without intramolecular potential, i.e., with $\epsilon/k_BT = 0$. As an illustrative example, we represent in Figure 2 the results obtained with $\epsilon/k_BT = 0$ and the fitted curve to the results for $\epsilon/k_BT = 0.3$ in the case of a chain with $N + 1 = 10$. Moreover, we have verified that for a chain of 10 elements the conformations

Table II
Results for $\langle S^2 \rangle$ Obtained at the Unperturbed State[a] with $\sigma/b = 0.8$ for Star Chains of Different Number of Arms[b]

F	N	$\langle S^2 \rangle$	g
2	19	4.15 ± 0.02	
2	25	5.6 ± 0.1	
2	37	8.45 ± 0.1	
2	49	11.0 ± 0.2	
2	55	12.3 ± 0.1	
6	19	2.28 ± 0.01	0.55 ± 0.01
6	37	4.39 ± 0.03	0.52 ± 0.01
6	49	5.64 ± 0.05	0.51 ± 0.01
12	25	2.08 ± 0.01	0.37 ± 0.01
12	37	2.95 ± 0.02	0.349 ± 0.003
12	49	3.84 ± 0.03	0.35 ± 0.01
18	19	1.56 ± 0.01	0.38 ± 0.01
18	37	2.46 ± 0.01	0.291 ± 0.002
18	55	3.48 ± 0.03	0.283 ± 0.005

[a] $\epsilon/k_BT = 0.3$ [b] $F = 2$ corresponds to linear chains.

Table III
Theoretical and Experimental Values of Ratio g for Long Star Chains of Different Functionalities

F	g_G[a]	g_{exptl}	g_{LJ}[b]	g_{LT}[c,e]
6	0.444	0.46[d]	0.49 ± 0.03	0.50
12	0.236	0.33[d] 0.28[f,g]	0.33 ± 0.02	0.35
18	0.160	0.23[f,g]	0.21 ± 0.01	0.28

[a] Theoretical values for Gaussian chains.[12] [b] Present calculations with intramolecular interactions. [c] Bibliographic results obtained by simulation in lattices. [d] Reference 16. [e] Reference 9. [f] Reference 18. [g] Reference 17 (for $F = 12$, the data correspond to the highest molecular weight).

generated with $\epsilon/k_BT = 0.3$ and $\sigma/b = 0.3$ closely follow the Gaussian distribution for the end-to-end distance

$$W(R) = 4\pi R^2(\tfrac{3}{2}\pi N b^2)^{3/2} \exp(-3R^2/2Nb^2) \qquad (14)$$

All these facts seem to indicate that the model obeys Gaussian statistics of intramolecular distances at $T = \Theta$. We are currently undertaking the study of distribution functions of R and S for the more realistic value of the LJ parameter $\sigma/b = 0.8$ in order to try to confirm this conclusion. In relation with this point, Fixman and Mansfield have recently stated[14] that all physically relevant moments of a chain with repulsive and attractive intramolecular potentials scale at the Θ point as a Gaussian chain in the limit $N \rightarrow \infty$.

Star Chains. We have obtained values of $\langle S^2 \rangle$ for star chains with the values of the LJ potential $\sigma/b = 0.8$ and $\epsilon/k_BT = 0.3$. Our goal has been to describe the dimensions of these chains by employing the same parameters that mimic the unperturbed conditions for linear chains. The results correspond to different types of chains, characterized by their number of arms, F. Table II summarizes these results. With the values of $\langle S^2 \rangle$ for a given type of star and those of a linear chain with the same number of beads, we have calculated the ratio g, also included in Table II. A linear regression analysis of the values of g for chains of different lengths vs. $1/N$ according to numerical methods in which uncertainties are considered[15] allows us to give a extrapolated estimation of g for a given chain in the limit $N \rightarrow \infty$. On the other hand, experimental studies of star-shaped polyisoprene in dioxane[16] and polystyrene in toluene[17] show that both linear and branched high molecular weight polymers have a common Θ temperature, though the temperature for which the second virial coefficient vanishes suffers a depression for highly branched chains of low molecular weights. Then, the extrapolated results corresponding to our values of the parameters can be compared with the bibliographic experimental data for g[16-18] obtained at the same temperature and solvent unperturbed conditions that apply to linear chains. We should also remark that the variation of ratio g with temperature is small, as current calculations that we are performing in the good solvent region and previous calculations of other authors[10] have pointed out. Then, the influence of the molecular weight and the degree of branching in the precise definition of the unperturbed temperature should not significantly change the values of g from our present estimations. The comparison between our final results for g and the experimental data is shown in Table III for F = 6, 12, and 18. The theoretical values corresponding to Gaussian molecules,[12] i.e., to chains without intramolecular interactions, are also included. Table III also contains simulation values obtained for the same star chains with lattice models.[9]

From the comparison of all these results, it can be concluded that only the introduction of an intramolecular potential in the model can describe the experimental data, since the Gaussian model yields very low values of g for high functionalities. Repulsion between units placed close to the star center is surely the cause of this poor performance of the model. As for the simulations with intramolecular interactions, it seems that the one described in this work is in a noticeably better accordance with the data than those performed on lattice models. However, we believe that differences are not high enough as to be attributed merely to the more realistic description of a polymer chain represented by our model, since the contribution of numerical treatments, especially extrapolation procedures, to the final results may be significant.

We have stressed above the great influence that finite size may have in the description of dimensions and their change with temperature in the case of linear chains. However, the significantly similar results for g obtained with very different values of N for each type of star chain (see Table II) indicate that our extrapolations can eliminate this effect. The only instance in which finite size yields an abnormal value of g is the $F = 18$, $N = 19$ chain, which contains only a bead per arm. In consequence, we believe that, though Monte Carlo simulations are performed on relatively short chains, most of the finite size influence on dimensions is common to the linear and branched chains, so that is not present in the ratio g (only weakly dependent on N). This allows us to perform extrapolations of these ratios to the high molecular weight limit with reasonable accuracy. Of course, repulsions between elements close to the star center are not eliminated, and these effects are responsible for the deviations of the present results from the values predicted by the Gaussian model. It should be considered, nevertheless, that both lattice simulation values[9,10] and experimental data[16-18] of high molecular weight samples also exhibit this deviation. Then, though our extrapolations cannot lead to the results of a infinitely long chain to which the Gaussian model is surely applicable (only a very small fraction of each arm would be affected by central repulsions), they are useful to describe the experimental results for real samples of high molecular weight polymers, for which the Gaussian model fails, as experimental data have consistently concluded.[16-18]

At any rate, we think that the agreement of our results with the data can be considered satisfactory. Nevertheless, most of our simulation results are still slightly higher than those obtained experimentally. The reason may be related to our assumption of a single value of the parameter σ/b for all the units in the chain. Since central theoretical units are surrounded by polymer material, they may be compelled to produce more compact arrangements of their internal bonds so that their interaction with neighboring units are repulsive only at shorter distances. A variable value of σ/b in our simulations, however, would distort the simplicity of the model, and, though it would improve the final results, it would probably not yield any further relevant information.

Acknowledgment. This work was supported in part by a grant from the Comisiôn Asesora de Investigaciôn Cientifica y Têcnica (Grant 1409/82).

References and Notes

(1) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981**, *32*, 433.
(2) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(3) Swislow, G.; Sun, S. T.; Nishio, I.; Tanaka T. *Phys. Rev. Lett.* **1980**, 44, 796.
(4) Sun, S. T.; Nishio, I.; Swislow, G.; Tanaka, T. *J. Chem. Phys.* **1980**, *73*, 5971.
(5) Vidakoviĉ, P.; Rondelez, F. *Macromolecules* **1984**, *17*, 418.
(6) McCrackin, F. L.; Mazur, J.; Guttman, C. M. *Macromolecules* **1973**, *6*, 859.
(7) Baumgärtner, A. *J. Chem. Phys.* **1980**, *72*, 871.
(8) Webman, I.; Lebowitz, J. L.; Kalos, M. H. *Macromolecules* **1981**, *14*, 1495.
(9) McCrackin, F. L.; Mazur, J. *Macromolecules* **1981**, *14*, 1214.
(10) Kolinñski, A.; Sikorski, A. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 3147.
(11) Freire, J. J.; Rey, A.; Garcia de la Torre, J. *Macromolecules*, following paper in this issue.
(12) Yamakawa, H. "Modern Theory of Polymer Solutios"; Harper and Row: New York, 1971.
(13) Pla, J. "Tesis de Licenciatura"; Universidad Complutense: Madrid, 1982.
(14) Fixman, M.; Mansfield, M. L. *Macromolecules* **1984**, *17*, 522.
(15) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969.
(16) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(17) Huber, K.; Burchard, W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 541.
(18) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.

Monte Carlo Calculations for Linear and Star Polymers with Intramolecular Interactions. 2. Nonpreaveraged Study of Hydrodynamic Properties at the Θ State

Juan J. Freire* and Antonio Rey

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain

José Garcia de la Torre

Departamento de Quimica Fisica, Facultad de Ciencias, Universidad de Murcia, 30001 Murcia, Spain. Received January 21, 1985

ABSTRACT: The hydrodynamic properties of linear and star polymers represented by a model with a Gaussian distribution of distances between neighboring elements and a Lennard-Jones potential to account for long-range interactions have been calculated by means of a Monte Carlo method based on the assumption of instantaneously rigid conformations and, therefore, free of preaveraging approximations. The results have been obtained for the value of the reduced temperature, which is shown in a preceding work to reproduce the unperturbed state of linear chains. Extrapolations to the long-chain limit give values of the hydrodynamic parameters P, Φ, and β that for linear chains are close to those obtained by similar calculations performed without the intramolecular potential. The results for stars at the same temperature are in fair agreement with experimental data of high molecular weight chains in Θ conditions, which could not be reproduced with less detailed theoretical treatments.

Introduction

The theoretical study of hydrodynamic properties of flexible chains in solution has generally made use of simple models in which intramolecular interactions are ignored or treated in a parametric way. Only very recently, several analytical[1,2] and simulation[2,3] treatments have considered a pairwise intramolecular potential, though these works are restricted to the study of translational properties calculated according to the Kirkwood approximation for the translational friction coefficient

$$f_t = \xi(N+1)^2\Big[\sum_{i=1}^{N+1}\sum_{j=1}^{N+1}\langle H_{ij}\rangle\Big]^{-1} \qquad (1)$$

where $N + 1$ is the number of hydrodynamic units of a chain and the terms H_{ij} depend on intramolecular distances R_{ij} according to

$$H_{ij} = (\pi/3)^{1/3} b h^* R_{ij}^{-1} \qquad \text{for } i \neq j$$
$$H_{ij} = 1 \qquad \text{for } i = j \qquad (2)$$

(b is the mean statistical length between neighboring units and h^* is a hydrodynamic parameter, proportional to ξ, the translational friction coefficient of the units,

$$h^* = \xi/(12\pi^3)^{1/2} b\eta_0 \qquad (3)$$

related also with the solvent viscosity η_0). In eq 1 $\langle\ \rangle$ means conformational average. These studies analyzed the value of R_h, the hydrodynamic radius for long chains. R_h is defined as

$$R_h = f_t/6\pi\eta_0 \qquad (4)$$

It should be pointed out, however, that the Kirkwood approximation does not seem to be sufficiently accurate in most cases, leading to values of f_t significantly different from those obtained experimentally for long flexible chains[4] or calculated in a nonpreaveraged way for certain types of rigid structures.[5]

When applied to linear Gaussian chains, the Kirkwood formula also gives results that differ significantly from those calculated by a Monte Carlo average over supposedly rigid conformations, treated individually and avoiding the orientational preaverage[6-8] method proposed recently by Zimm.[6] Though possible coupling of hydrodynamic in-

0024-9297/86/2219-0457$01.50/0 © 1986 American Chemical Society