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Perturbation Expansion of Macromolecules in Solution at the Θ-State

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ABSTRACT: By means of Monte Carlo methods the binary interaction terms up to the third order and the ternary interaction term of the perturbation expansion were calculated for model chains on a simple cubic lattice at the Θ-state (the second osmotic virial coefficient $A_2 = 0$) and at the state of vanishing binary interactions ($\beta_2 = 0$). The following results were obtained: (a) theories on A_2 that are based solely on binary interaction terms fail in the vicinity of the Θ-state; (b) even at the Θ-state the configurational properties of a polymer chain cannot be described properly by a third-order perturbation theory; and (c) chains with $\beta_2 = 0$ do not exhibit pseudoideal behavior.

Introduction

The cluster expansion method of the perturbation theory was pioneered by Teramoto[1] and Fixman.[2] More recently this expansion has been reformulated by passing from the discrete model to a continuum limit.[3,4] In each of these developments the reference system is taken to be a random-flight chain which was frequently identified with a real chain on Θ-point conditions. The potential of mean force between the structural units of the chain is generally described by δ-function type interactions. In this case the binary cluster integral β_2 can be factored out and the distribution function may be expressed as a power series in β_2 if ternary and higher order cluster terms are ignored. Although Edwards[5] could show that these expansions are not convergent but asymptotic, they were still used to study the behavior of polymer solutions in the vicinity of the Θ-point because the distribution of a random-flight chain is reobtained if β_2 vanishes. On the other hand, this is a range where the two-parameter theory fails, since terms containing the ternary cluster integral β_3 can no longer be neglected if β_2 is small. From experimental data the ternary interaction parameter is estimated to be positive near the Θ-point.[6] Therefore the sum of the binary cluster terms has to be negative to compensate the influence of the ternary ones.

So far the problems arising with calculations in the vicinity of the reference state have been discussed. They become even more intricate at the Θ-point. As has been pointed out in an earlier publication,[7] the most appropriate definition of the Θ-state both from the theoretical and from the practical viewpoint is the vanishing of the second osmotic virial coefficient, A_2. On this basis it can be shown by comparison of various configurational properties that the Θ-state thus defined is not identical with a random-flight state, contradicting the statements of Flory.[8] After all, it seems to be desirable to get an impression of the magnitude of the first few terms of the perturbation expansion at the Θ-state ($A_2 = 0$) and at the state $\beta_2 = 0$ and to investigate to what extent configurational properties (for example, the mean square end-to-end distance $\langle h^2 \rangle$) can be reproduced by a third-order theory.

Basic Equations and Model

The starting point is the perturbation expansion, which is formulated similar to that of Fixman.[2] According to this theory the mean square end-to-end distance $\langle h^2 \rangle$ is given by

$$\frac{\langle h^2 \rangle}{nl^2} = \frac{1 - N_1 + N_2 - N_3 + \dots}{1 - D_1 + D_2 - D_3 + \dots} = 1 + T_1 - T_2 + T_3 - + \dots \quad (1)$$

with

$$N_1 = \frac{1}{nl^2}\sum_{i<j}\int \chi_{ij} r_n^2 P_0(\vec{r}_{ij},\vec{r}_n)\, d\vec{r}_{ij}\, d\vec{r}_n = \frac{1}{nl^2}\langle \sum_{i<j} \chi_{ij} r_n^2 \rangle_0 \quad (2a)$$

$$N_2 = \frac{1}{nl^2}\sum_{i<j}\sum_{k<l}{}'\int \chi_{ij}\chi_{kl} r_n^2 P_0(\vec{r}_{ij},\vec{r}_{kl},\vec{r}_n)\, d\vec{r}_{ij}\, d\vec{r}_{kl}\, d\vec{r}_n = \frac{1}{nl^2}\langle \sum_{i<j}\sum_{k<l}{}' \chi_{ij}\chi_{kl} r_n^2 \rangle_0 \qquad (i \le k) \quad (2b)$$

$$N_3 = \frac{1}{nl^2}\sum_{i<j}\sum_{k<l}\sum_{p<q}{}'\int \chi_{ij}\chi_{kl}\chi_{pq} r_n^2 P_0(\vec{r}_{ij},\vec{r}_{kl},\vec{r}_{pq},\vec{r}_n)\, d\vec{r}_{ij}\, d\vec{r}_{kl}\, d\vec{r}_{pq}\, d\vec{r}_n = \frac{1}{nl^2}\langle \sum_{i<j}\sum_{k<l}\sum_{p<q}{}' \chi_{ij}\chi_{kl}\chi_{pq} r_n^2 \rangle_0 \qquad (i \le k \le p) \quad (2c)$$

$$D_1 = \sum_{i<j}\int \chi_{ij} P_0(\vec{r}_{ij})\, d\vec{r}_{ij} = \langle \sum_{i<j} \chi_{ij} \rangle_0 \quad (2d)$$

$$D_2 = \sum_{i<j}\sum_{k<l}{}'\int \chi_{ij}\chi_{kl} P_0(\vec{r}_{ij},\vec{r}_{kl})\, d\vec{r}_{ij}\, d\vec{r}_{kl} = \langle \sum_{i<j}\sum_{k<l}{}' \chi_{ij}\chi_{kl} \rangle_0 \qquad (i \le k) \quad (2e)$$

$$D_3 = \sum_{i<j}\sum_{k<l}\sum_{p<q}{}'\int \chi_{ij}\chi_{kl}\chi_{pq} P_0(\vec{r}_{ij},\vec{r}_{kl},\vec{r}_{pq})\, d\vec{r}_{ij}\, d\vec{r}_{kl}\, d\vec{r}_{pq} = \langle \sum_{i<j}\sum_{k<l}\sum_{p<q}{}' \chi_{ij}\chi_{kl}\chi_{pq} \rangle_0 \qquad (i \le k \le p) \quad (2f)$$

$P_0(\vec{r}_{ij}, \dots, \vec{r}_{st})$ means the unperturbed multivariate distribution function of $\vec{r}_{ij}, \dots, \vec{r}_{st}$. n and l are the bond number

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Table I
n Dependence of the Reciprocal Reduced Temperature and of the End-to-End Distance for Which $A_2 = 0$

n	Φ_Θ	$\langle h^2\rangle/(nl^2)$	n	Φ_Θ	$\langle h^2\rangle/(nl^2)$
8	0.2363	1.461	24	0.2494	1.627
10	0.2392	1.501	36	0.2532	1.671
12	0.2417	1.528	64	0.2574	1.738
16	0.2452	1.567	128	0.2608	1.778

and the bond length, respectively. The mean square end-to-end distance of the reference state is presumed to be

$$\langle h^2\rangle_0 \equiv \int r_n^2 P_0(\vec{r}_n)\, d\vec{r}_n = nl^2 \tag{3}$$

and

$$\chi_{ij} = 1 - \exp[-w(r_{ij})/(kT)] \tag{4}$$

with the potential of mean force $w(r_{ij})$ between the structural units i and j. The primed summation follows the rules of the cluster theory (i.e., any term is ignored (1) in which two factors have an index pair in common or (2) which has already been taken into account with permutated factors). The indices in eq 1 indicate the number of contacts that have been considered for their calculation.

Thus the T terms can be expressed as

$$T_1 = D_1 - N_1 \tag{5a}$$

$$T_2 = D_2 - N_2 + D_1N_1 - D_1^2 \tag{5b}$$

$$T_3 = D_3 - N_3 + D_2N_1 - 2D_1D_2 + D_1N_2 - D_1^2N_1 + D_1^3 \tag{5c}$$

The triple-contact term T_3 comprises terms with three binary interactions and such with one ternary interaction symbolized by T_3^*

$$T_3^* = D_3^* - N_3^* \tag{6a}$$

with

$$D_3^* = \langle \sum_{i<j<k} \chi_{ij}\chi_{ik}\chi_{jk}\rangle_0 \tag{6b}$$

and

$$N_3^* = \frac{1}{nl^2}\langle \sum_{i<j<k} \chi_{ij}\chi_{ik}\chi_{jk}r_n^2\rangle_0 \tag{6c}$$

Subtracting T_3^* from T_3 we obtain $\tilde{T}_3$, which contains binary interaction terms only.

$$\tilde{T}_3 = T_3 - T_3^* \tag{6d}$$

The N and D terms (eq 2 and 6) were calculated by a Monte Carlo method. Since the averages have to be taken over an ensemble of unperturbed chains, a random-flight walk on a simple cubic lattice (six choices) was used as the model. It satisfies the condition given in eq 3. Samples of chains were generated for several values of n (8, 10, 12, 16, 24, 36, 64, and 128) with a size of 10^5 members (n = 8 and 10) and 10^6 members (otherwise). After the generation of any chain, the numbers of contacts (two neighboring lattice sites are occupied by nonbonded structural units of the chain) and of intersections (two units occupy the same lattice site) were counted. The corresponding values of χ_{ij} were calculated by eq 4. As in ref 7 a kind of square well potential is used for $w(r_{ij})$ ($j \geq i + 2$) that (1) goes to infinity if the units i and j intersect, (2) assumes the value w if i and j form a contact, and (3) vanishes otherwise. Since it is intended to investigate the perturbation expansion at the Θ-state, the values of $w/(kT)$ ($=\Phi_\Theta$) have to be taken so as to nullify A_2. They are known from previous work[7] and are listed together with $\langle h^2\rangle$ in Table I. Thus χ_{ij} is given by

$$\begin{aligned}\chi_{ij} &= 1 \quad \text{if } \vec{r}_i = \vec{r}_j \\ &= 1 - \exp(\Phi_\Theta) \quad \text{if } |\vec{r}_j - \vec{r}_i| = l \\ &= 0 \quad \text{otherwise}\end{aligned}$$

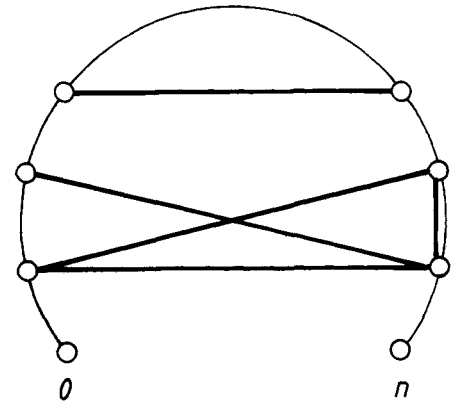

Figure 1. Cluster diagram of an exemplary chain configuration.

As can be seen, only those pairs contribute to the N and D terms that intersect or are nearest neighbors. If a chain has one interference (contact or intersection), it contributes one term each to D_1 and N_1 (multiplied with the squared end-to-end distance in the latter case). A chain with two interferences contributes two terms each to D_1 and N_1, one term each to D_2 and N_2, etc. Chains with three interferences and more were tested if they exhibit ternary clusters, i.e., interferences between the units i and j, j and k, and i and k. The corresponding terms were summed in D_3^* and N_3^*. Owing to the model, there are two types of ternary interactions: (1) three structural units occupy the same lattice site, and (2) two units intersect and a third one is located on a neighboring site. Of course this third unit must not be as well a chain neighbor of the intersecting units. An example may illustrate the course of the calculations: In Figure 1 Yamakawa's representation[9] of a chain configuration is depicted, which might have been obtained by a Monte Carlo run. The circular arc represents the chain, whereas the straight lines symbolize the interferences described above. This configuration contributes five terms to D_1 and N_1, ten terms to D_2 and N_2, one term to D_3^* and N_3^*, and nine terms to $\tilde{D}_3$ and $\tilde{N}_3$. The sums of the respective terms are identical with the sums appearing in eq 2 and 6. They have to be averaged over all configurations of the sample.

Results and Discussion

Figure 2 displays the dependence of the terms T_1, T_2, $\tilde{T}_3$, and T_3^* on the number of bonds (scaled as $n^{-1/2}$). For short chains the terms are relatively small, but they change considerably with incresing n. Finally T_1 and $\tilde{T}_3$ assume negative values and T_2 and T_3^* positive values. The curves of T_1 and T_3^* are smooth as contrasted with the curves of T_2 and $\tilde{T}_3$, which exhibit sudden changes in the range of $n \sim 100$. As could be expected all the terms diverge for $1/n \to 0$. It is, however, known from theoretical work with δ-function type interactions[2,10,11] that the T terms in the asymptotic limit are of the form $T_i = A_i n^{\nu_i}$, with ν_i = 0.5, 1.0, 1.5, and 0.5 for i = 1, 2, $\tilde{3}$, and 3*, respectively. This opens the possibility to obtain A_i by an extrapolation of the plots T_i/n^{ν_i} against, say, $n^{-1/2}$. Each of the data sets was fitted to a kth-order polynomial by the method of least squares. The proper value of k was found by the F test. The results are shown in Figure 3. The standard deviations were always smaller than 4×10^{-3}. The corre-

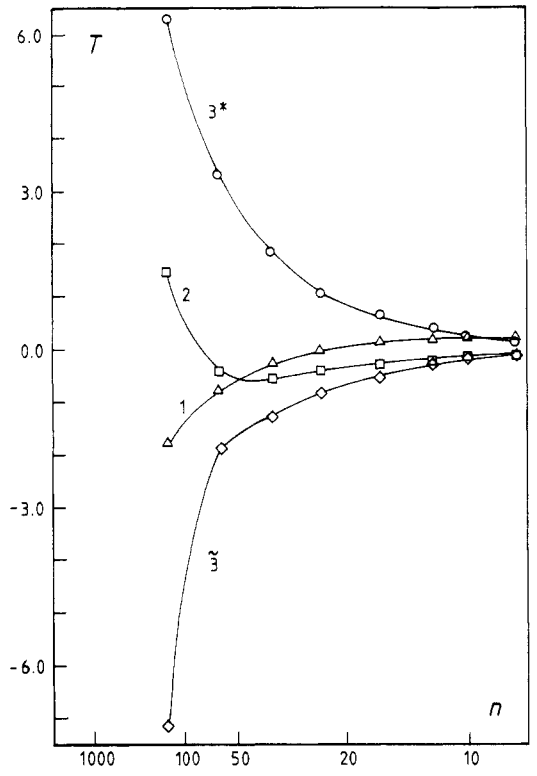

Figure 2. Dependence of the terms of the perturbation expansion on the number of bonds (the abscissa is scaled as $n^{-1/2}$). The numbers near the curves symbolize the indices i in T_i.

Table II
Some Terms of the Perturbation Expansions, T_i, in the Asymptotic Limit ($A_2 = 0$) with $z_2 = (1.5/\pi)^{3/2}(\beta_2/l^3)n^{1/2}$ and $z_3 = (1.5/\pi)^3(\beta_3/l^6)n^{1/2}$

i	this work	analytical work[9,11,16]
1	$(-0.3780 \pm 0.0081)n^{1/2}$	$1.333z_2$
2	$(0.1754 \pm 0.0178)n$	$2.075z_2^2$
$\tilde{3}$	$(-0.002682 \bullet 0.000096)n^{3/2}$	$6.279z_2^3$
3*	$(1.017 \pm 0.010)n^{1/2}$	$6.966z_3$

sponding error bars would not exceed the size of the symbols used and were, therefore, not plotted. The asymptotic values of the terms T together with their standard deviations are listed in Table II.

Since it is well-known that binary interaction terms are universal in nature,[12,13] it is useful to compare them with those of the δ-function approach. The corresponding expressions are given in the last column of Table II. The ternary interaction terms are also included. The terms, gained by theory, can be used to test the reliability of the extrapolation procedure. Introducing them into the ratios T_2/T_1^2 and $\tilde{T}_3/T_1^3$, one obtains $2.075/1.333^2 = 1.168$ and $6.279/1.333^3 = 2.651$, respectively. The corresponding values for the extrapolated terms are 1.228 ± 0.098 and 0.050 ± 0.001. The former value is exact within the error limits, thus confirming the goodness of the extrapolation, whereas the latter is much too small. The theoretically predicted ratio would be obtained if $\tilde{T}_{3,\mathrm{red}} = -0.141$. The reason for the bad agreement may be that the chains considered are still too short to allow a reliable extrapolation in each case. As already mentioned above, the double- and triple-contact terms are nearly constant for $n < 100$. Above this range the T_2 line becomes more curved, and it is possible that the same is valid for the $\tilde{T}_3$ line, but for still larger values of n.

From T_1 the value of the binary cluster integral can be extracted, and it is found to be $\beta_2/l^3 = -0.860$. This value should be identical with that found by a short analytical

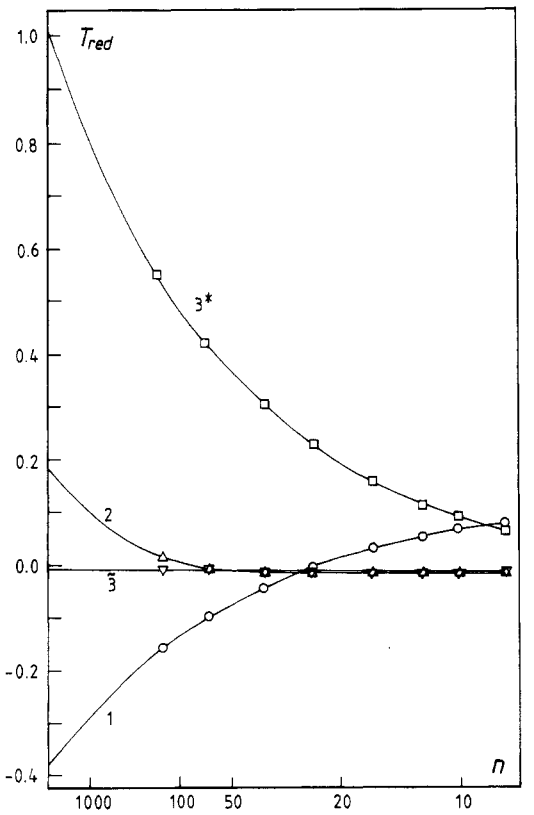

Figure 3. Dependence of the reduced terms of the perturbation expansion on the number of bonds. For further details see the caption of Figure 2 and the text.

calculation: for lattice models the binary cluster integral can be converted to

$$\beta_2/l^3 = \sum_j \{1 - \exp[-w_j/(kT)]\} \tag{7}$$

The summation goes over all possible configurations of two segments on the lattice with one segment fixed. Corresponding to the model, only such configurations contribute to the sum where the two segments are on the same ($w_j \to \infty$) lattice site or are neighbors [$w_j/(kT) = -\Phi_\Theta$]. Therefore $\beta_2/l^3 = 1 + 6[1 - \exp(\Phi_\Theta)]$, and $\beta_2/l^3 = -0.8543$ is obtained with good agreement to the extrapolated value. The fact that β_2 is different from zero at the Θ-state proves that any two-parameter theory for A_2 is unsuited in the vicinity of $A_2 = 0$ because these theories predict that A_2 is proportional to β_2, i.e., A_2 vanishes only if $\beta_2 = 0$.

In contrast to the binary interaction terms, the ternary ones are not universal (i.e., they depend on the potential) as has already been demonstrated.[11] It makes, therefore, no sense to compare T_3* with the corresponding theoretical expression, since the two terms have been obtained from different models. On the other hand, T_3* can be used to test a perturbation theory that was published only recently.[4] The authors, considering binary and ternary interactions, derived (among others) the following equations:

$$\langle h^2\rangle/\langle h^2\rangle_0 = 1 + z_2[4/3 - 8/(\pi\sigma)] + 4z_3^0(4\sigma/3 - \pi - 8/\pi) + \ldots \tag{8}$$

$$A_2 = \text{const} \times [z_2 + 8z_3^0(\sigma/2 - 1)] \tag{9}$$

σ is proportional to $n^{1/2}$ and depends on the model, whereas $z_3^0 = z_3/n^{1/2}$ (z_3 is defined in the caption of Table II).

Defining the Θ-state by $A_2 = 0$, the authors obtained from eq 9

$$z_2 + 8z_3^0(\sigma/2 - 1) = 0 \tag{10}$$

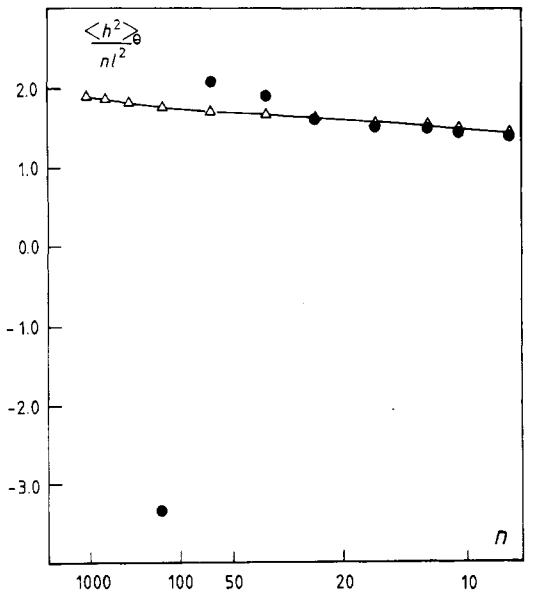

Figure 4. Monte Carlo data of the characteristic ratio at the Θ-state vs. number of bonds: "exact" data (△); data of the third-order perturbation theory (●).

The insertion of z_2 in eq 8 gives an expression that depends on z_3^0 only. Because of the lack of reliable data the authors used a rough estimation for z_3^0 and found a good agreement between theory and the Monte Carlo data of ref 7. Knowledge of T_3^* allows us now to test the theory in a more profound way. Since the second term on the right-hand side of eq 8 is equivalent to T_1, the third one to T_3^*, the validity of the theory can be verified if it can be shown that eq 8 and 9 are consistent. In the asymptotic limit ($\sigma \gg 1$) the following associations can be deduced:

$$-0.3780n^{1/2} = T_1 \leftrightarrow 4z_2/3 \tag{11}$$

$$1.017n^{1/2} = T_3^* \leftrightarrow 16\sigma z_3^0/3 \tag{12}$$

The terms on the left-hand sides of eq 11 and 12 have been obtained for $A_2 = 0$. According to eq 10 they should cancel on addition. This, however, does not happen; the validity of the theory cannot be confirmed. Of course, this test rests on the reliability of the extrapolation of T_3^*.

Now the question is treated to which accuracy configurational properties at the Θ-state can be calculated if only a few terms of the perturbation expansion are taken into account. For this purpose $\langle h^2 \rangle / (nl^2)$ is evaluated by means of eq 1, that is, terms up to the third order only are considered. Figure 4 displays the results. The open triangles connected by a curve are Monte Carlo data from a previous calculation (see Table I), while the filled circles are the data obtained by eq 1. As can be seen, the agreement between the two data sets is good only for short chains, where higher contact terms are of minor importance. For long chains, however, the deviations are very high, and in one case a physically unrealistic negative value is obtained. This shows that even at the Θ-state the contributions of higher contact terms of the perturbation expansion cannot be neglected.

As a last topic the configurational properties are investigated at a state for which $T_1 = 0$. At this state the binary interactions vanish in the asymptotic limit, i.e., $\beta_2 = 0$. The properties of the chain are now determined by ternary (and higher order) interactions only. The values of Φ that nullify T_1 were found by Monte Carlo calculations which were performed for several n. A plot of the results is given in Figure 5. For $n > 15$ the data points can be fitted with high accuracy by a second-order polynomial.

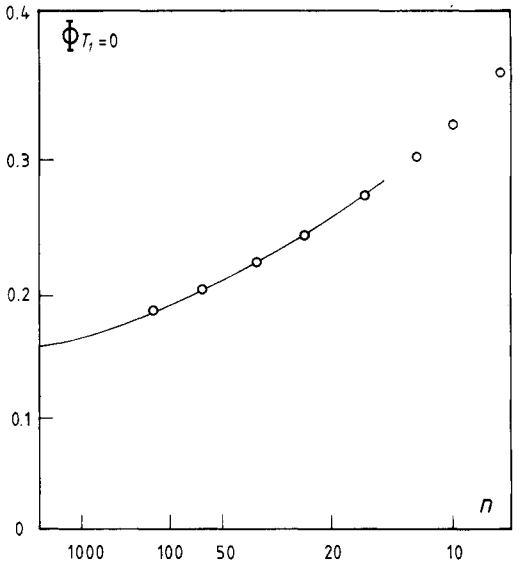

Figure 5. Plot of exp(Φ) vs. $n^{-1/2}$. Φ is the reduced potential for which $T_1 = 0$.

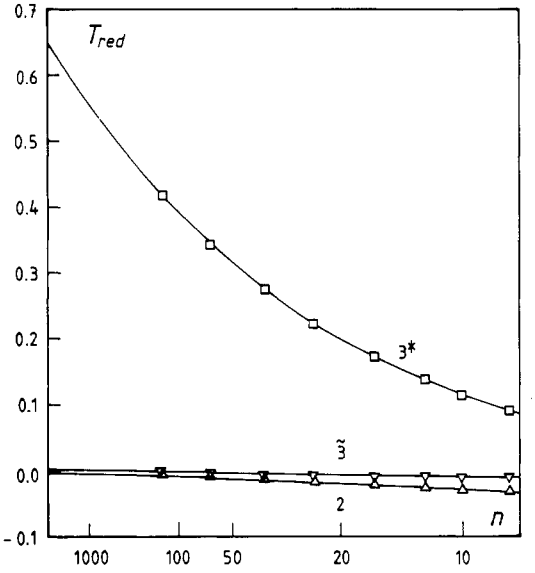

Figure 6. Dependence of the reduced terms of the perturbation expansion on the number of bonds if $T_1 = 0$. Further details are given in the caption of Figure 2.

Table III
Characteristic Data of a Model Chain on a Simple Cubic Lattice[a]

Φ	$T^* = \Phi^{-1}$	γ	remarks
0	∞	6/5	hard-sphere interaction
0.1542	6.49	~6/5	vanishing binary interactions
0.2693	3.71	1	$A_2 = 0$, Θ-state
>0.2693	<3.71	2/3	collapsed chain

[a] For details see text.

By extrapolation to $n^{-1/2} = 0$ the asymptotic value $\Phi(\beta_2 = 0) = 0.1608$ is obtained, which is near $\Phi = 0.1542$ calculated by using eq 7. After that T_2, $\tilde{T}_3$, and T_3^* were calculated, and the properly reduced terms were fitted by polynomials in a way similar to that described above (Figure 6).

The terms $T_{2,red}$ and $\tilde{T}_{3,red}$ that contain only binary interactions vanish for $1/n \to 0$ in accordance with the theory, whereas the ternary interaction term $T_{3,red}^*$ is different from zero. The configurational properties at this state are demonstrated by the example of the mean-square

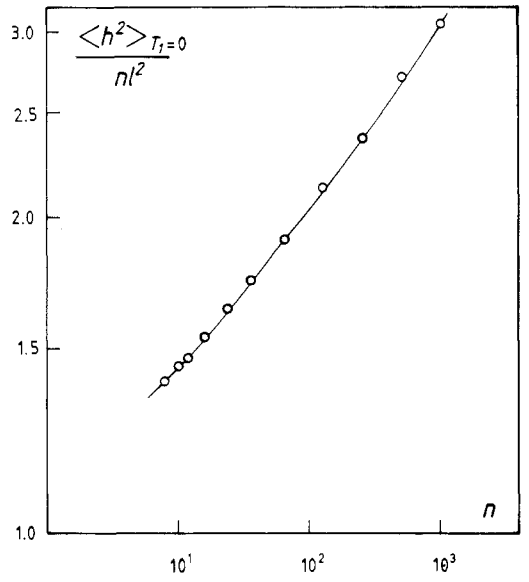

Figure 7. Double-logarithmic plot of $\langle h^2 \rangle / (nl^2)$ vs. n if $T_1 = 0$.

end-to-end distance. This quantity was evaluated by Monte Carlo methods for some values of n and plotted against n in a double-logarithmic fit (Figure 7).

As can be seen, the ratio $\langle h^2 \rangle / (nl^2)$ diverges, thus indicating that polymer chains at the state of vanishing binary interactions are not pseudoideal. The shape of the curve suggests that it may become linear for $n \to \infty$. If so, the asymptotic relation $\langle h^2 \rangle \sim n^\gamma$ is obeyed. A rough estimation of the slope of the nearly linear part of the curve ($n > 150$) gives $\gamma = 1.17$. This value nearly equals the exponent obtained for hard-sphere chains (1.18).

Table III gives a brief summary of the characteristic data of chains on a simple cubic latice with repulsive and various attractive forces.

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Monte Carlo Calculations for Linear Chains and Star Polymers with Intramolecular Interactions. 3. Dimensions and Hydrodynamic Properties in Good Solvent Conditions

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ABSTRACT: The dimensions and reduced hydrodynamic properties of linear and several types of star polymers with differing numbers of units, N, have been calculated by averaging over samples of Monte Carlo simulated conformations, using a chain model that considers Gaussian distribution of distances between neighboring units and a Lennard-Jones (LJ) potential to describe the intramolecular interactions. The LJ parameters have been set so that they are able to reproduce the good solvent conditions. The hydrodynamic parameters P, Φ, and β have been calculated together with the ratios g, h, and g' of the properties of the star chains to those of linear chains with the same values of N. Extrapolation to high molecular weights has been performed, and the estimates have been analyzed and compared with previously reported theoretical and experimental results. Our values are extended to stars with many arms for which previous theoretical calculations are not available, and they can be considered to be in good agreement with the experimental data.

Introduction

The study of the dimensions and hydrodynamic properties of flexible polymers in solution has attracted much attention recently from both theoretical and experimental points of view. The influence of the solvent quality (and temperature) on the dimensions of linear chains has been investigated in the "good solvent region", in unperturbed or Θ conditions, and also in the case of systems with temperature below the Θ point.[1-3] The measurement and prediction of the hydrodynamic properties of linear flexible polymers in all these regions have been the goal of many studies,[1-7] while the basis of the theoretical treatment of these properties has been revised and improved.[8-10] Moreover, the recent synthesis of well-characterized samples of starlike polymers with a high number, $F > 6$, of uniform arms, by Roovers et al., has caused an increasing interest in the understanding of the properties of these particular molecules. Thus, these systems have been the object of many experimental[11-14] and theoretical[15,16] investigations, as well as detailed numerical calculations.[17-23]

In previous work we have performed theoretical calculations for the dimensions[24] and hydrodynamic properties[25]

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