Relations between Averaged Configurational Properties of Linear and Starlike Polymer Models at the Θ Temperature†

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ABSTRACT: It is known from earlier work that static properties of polymer molecules at the Θ state do not obey any of the theoretical expressions derived for that case. By means of Monte Carlo calculations on lattice walks, it could be established in this investigation that the ratios of the mean values of some configurational quantities are nevertheless very close to those gained by Gaussian statistics. The Θ-point depression by branching observed experimentally could be confirmed.

Introduction

Unperturbed chains are not equivalent to chains at the Θ state, because long-range interactions are not considered for the former, whereas they do exist for real chains at the Θ state even if attractive and repulsive forces are balanced properly so that the second osmotic virial coefficient, A_2, vanishes, and the system obeys van't Hoff's law. This point of view is supported by theoretical investigations of Duplantier,[1,2] who found that the mean-square end-to-end distance of a chain at the Θ temperature is not the same as the "unperturbed" mean-square end-to-end distance. Furthermore, several Monte Carlo studies[3-7] have shown that the configurational properties of a dissolved polymer molecule at the Θ state cannot be described properly by the existing theories based on models with short-range interferences, the calculated values always being greater than those predicted by theory. Because of the significant difference between a chain at the Θ state and a chain unperturbed by long-range interactions, it is of interest to get some insight to what extent the dimensionless ratios of configurational properties are affected, when passing from an unperturbed (Gaussian) model to a molecule at the Θ state and to answer the question of whether the latter can still be described by Gaussian statistics. These ratios can be evaluated analytically for unperturbed chains, and they have to be taken in the asymptotic limit, in order to clear them from parameters reflecting the local microscopic features of the chains. The corresponding quantities of the chains at the Θ temperature (defined by $A_2 = 0$) were calculated by Monte Carlo methods. During the past 2 decades other authors have also evaluated some of these ratios, but they determined the Θ temperature by the relation $\langle R^2 \rangle \propto n$, i.e., the proportionality between the mean-square end-to-end distance (or the mean-square radius of gyration) and the number of segments comprising the polymer. Both definitions can be assumed to be equivalent, but the latter is only valid in the asymptotic limit in most cases. Molecules, however, that can be created by Monte Carlo methods are relatively short ($n < 1000$). This might be a range where the data even of a Θ molecule do not yet follow the relation $\langle R^2 \rangle \propto n^{2\nu}$ with $2\nu = 1$, but with 2ν different from unity.

Model and Equations

The polymer molecules are simulated by nonintersecting walks on a five-choice cubic lattice. A linear chain consists of n steps (bonds) of length l (lattice spacing) each and occupies, therefore, $n + 1$ lattice sites. An interaction energy, w, is attached if two nonbonded segments of the chain form a contact; i.e., they are separated by one lattice spacing. It should be pointed out that these "energies" have to in fact be considered as potentials of mean force, which depend on the temperature and on the activity of the solvent inherent in the model. The total potential of mean force of a given configuration is calculated by application of the superposition approximation

$$W = \sum_{i<j} w(\mathbf{r}_{ij})$$

with

$$w(\mathbf{r}_{ij}) = \begin{cases} \infty & \text{if } \mathbf{r}_i = \mathbf{r}_j \text{ and } i \neq j \\ -w & \text{if } |\mathbf{r}_i - \mathbf{r}_j| = l \text{ and } |j - i| \neq 1 \\ 0 & \text{otherwise} \end{cases}$$

Star molecules of uniform distribution are constructed by combining f (=4–6) linear chains of equal lengths originating from the same lattice site.

To study the configuration of these models at the Θ state, a value of $\Phi \equiv \beta w$ has to be found that nullifies A_2. As has earlier[5] been shown, A_2 can be obtained from

$$\frac{A_2}{l^3} = \frac{\sum_i \sum_j \exp\{-\beta[W_1(i) + W_1(j)]\} \sum_p \{1 - \exp[-\beta W_{12}(p|i,j)]\}}{2(n+1)^2 \sum_i \sum_j \exp\{-\beta[W_1(i) + W_1(j)]\}}$$

with $\beta = 1/(kT)$.

The symbols have the following meaning: $W_1(i)$ and $W_1(j)$ are the intramolecular potentials of mean force of two molecules that are in the (internal) configurational states i and j, respectively. $W_{12}(p|i,j)$ is the intermolecular potential of mean force between the two molecules, which are in the (external) relative position p to each other, given the respective (internal) states i and j. The summations extend over all possible configurations and relative positions of the two molecules.

In this work the summation over i and j was not performed over the whole population of configurations but only over the relatively small sample of 50 000 chain pairs generated by a plain Monte Carlo method. Further details of the calculation can be found in ref 6. For the values of Φ_Θ thus obtained, the n dependence of the following quantities was investigated:

(i) $\langle R^2 \rangle / \langle S^2 \rangle$, the ratio of the mean-square end-to-end distance and the mean-square radius of gyration. Its Gauss-

† Dedicated to Professor Dr. W. Burchard on the occasion of his 60th birthday.

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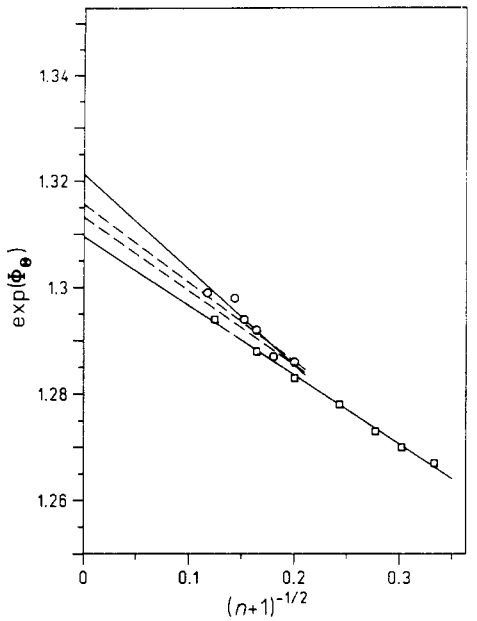

Figure 1. Plot of exp Φ_Θ versus $(n + 1)^{-1/2}$ for linear chains (-□-) and stars with functionality $f = 6$ (-○-). Broken lines (without symbols): stars with $f = 4$ and $f = 5$ (from below).

ian value is 6.

(ii) $g = \langle S^2\rangle_s/\langle S^2\rangle_l$, the ratio of the mean-square radius of gyration of a star molecule (s) to that of a linear chain (l) comprising the same number $(n + 1)$ of segments. g depends on the functionality f of the star, with the Gaussian value[8] $g = 3/f - 2/f^2$.

(iii) $\delta_{4,2}{}^s = \langle S^4\rangle/\langle S^2\rangle^2$, reduced moment, for Gaussian molecules assuming the values[9,10] 19/15 (linear) and $(135 - 120/f + 4/f^2)/[15(3 - 2/f)^2]$ (stars), respectively.

(iv) $\langle S^2\rangle^{1/2}\langle 1/R\rangle$, $\langle 1/R\rangle$ is the reciprocal hydrodynamic radius in the Kirkwood approximation. Its Gaussian value is $8/(3\pi^{1/2})$ (linear) and $8(3 - 2/f)^{1/2}[1 + (f - 1)(2^{1/2} - 1)]/(3f\pi^{1/2})$ (stars).[11]

(v) $\langle l_1^2\rangle:\langle l_2^2\rangle:\langle l_3^2\rangle$, the ratios of the principal orthogonal components of $\langle S^2\rangle$. Since analytical expressions for the corresponding Gaussian molecules are not known yet, Monte Carlo data obtained from random walks are used. All these quantities were calculated by the Monte Carlo technique of biased sampling[12] with sample sizes of 10^5.

Results and Discussion

Figure 1 displays the dependence of the reduced Θ temperature, in terms of exp Φ_Θ, on the number of segments for linear and starlike molecules. The data of the linear chains have been taken from former publications.[5,13] Although the sample sizes were equally large for each model, the degree of linear correlation is obviously best for the data points of the linear chain, whereas a certain scattering of the data points of the stars occurs, which increases with the functionality of the branching point. The respective correlation coefficients, obtained by linear regression, are -0.9997 (linear), -0.9871 ($f = 4$), -0.9632 ($f = 5$), and -0.9555 ($f = 6$). To avoid cluttering, the data points of the stars with $f = 4$ and $f = 5$ are omitted; only the (dashed) straight regression lines are shown. As can be noticed, the reduced Θ temperatures differ somewhat, in accordance with experimental observations,[14-20] where a depression of the Θ point by branching has been established. The asymptotic values of Φ_Θ obtained by extrapolation are 0.2693 ± 0.0002 (l), 0.2723 ± 0.0014 ($f = 4$), 0.2731 ± 0.0025 ($f = 5$), and 0.2791 ± 0.0035 ($f = 6$). Several authors,[7,21] who have investigated

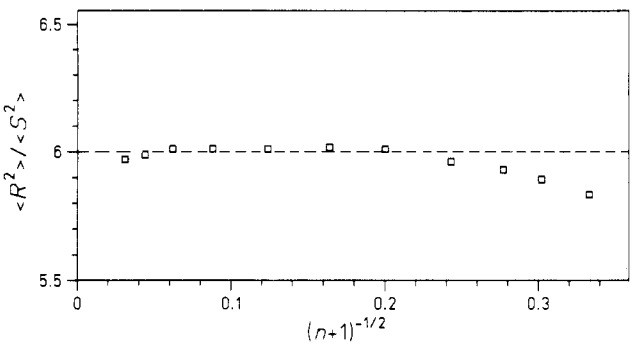

Figure 2. Dependence of the ratio $\langle R^2\rangle/\langle S^2\rangle$ on the number of segments.

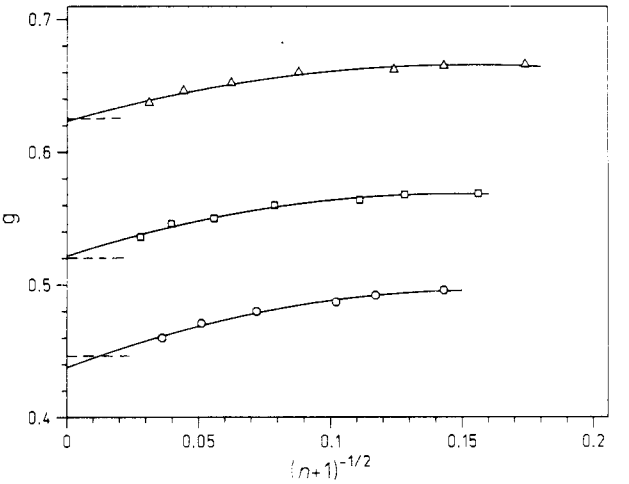

Figure 3. Dependence of the ratio $g = \langle S^2\rangle_s/\langle S^2\rangle_l$ on the number of segments. The stars have the functionality $f = 4$ (-△-), $f = 5$ (-□-), and $f = 6$ (-○-). The dashed lines indicate the Gaussian values.

stars, assumed the Θ point to coincide with that of the corresponding linear system and estimated $\Phi_\Theta = 0.275$ for star-shaped molecules independent of the functionality. This value agress roughly with those found here.

The dependence of the ratio $\langle R^2\rangle/\langle S^2\rangle$ on the number of segments is shown in Figure 2. The data approaches the Gaussian value within the standard deviation (0.003) if $n > 20$.

The value of g for uniform stars has been calculated by simulation methods in a lot of studies,[21-31] with some of them[21-23,26,30] giving results for the Θ point. They all found g ratios that were 0.02–0.05 greater than the corresponding Gaussian values. These outcomes are not confirmed by our results, as illustrated in Figure 3. An F test proved that the data could properly be fitted by the function

$$g = a + b(n + 1)^{-1/2} + c(n + 1)^{-1} \qquad (1)$$

The asymptotic values for g obtained from the intercept of the extrapolated lines are summarized in Table I. As can be seen, the g ratios for the Θ state are very close to the Gaussian values. The difference between these results and those found by other workers is surely due to the method applied for the determination of Φ_Θ. This is obviously a subtle problem that can only be treated adequately by using the condition $A_2 = 0$.

The reduced moment $\delta_{4,2}{}^s = \langle S^4\rangle/\langle S^2\rangle^2$ at the Θ point for linear and starlike molecules has been determined by Mazur and McCrackin.[21] They found deviations from the Gaussian values from 0.01 to 0.02. Our data, shown in Figure 4, were fitted to a function similar to eq 1. The agreement between the asymptotic values of $\delta_{4,2}{}^s$ (Table I) and those of Mazur and McCrackin is perfect. In

Table I
Asymptotic Values of Various Ratios of Static Properties for Gaussian and Θ-State Molecules

	linear	star		
		$f = 4$	$f = 5$	$f = 6$
$\langle S^2\rangle_s/\langle S^2\rangle_l$				
RW[a]		0.625	0.520	0.444
Θ		0.623 ± 0.004	0.522 ± 0.003	0.438 ± 0.004
$\langle S^4\rangle/\langle S^2\rangle^2$				
RW[a]	1.267	1.123	1.096	1.079
Θ	1.257 ± 0.004	1.112 ± 0.004	1.084 ± 0.004	1.069 ± 0.004
$\langle S^2\rangle^{1/2}\langle 1/R\rangle$				
RW[a]	1.505	1.334	1.289	1.258
Θ	1.479 ± 0.002	1.298 ± 0.003	1.256 ± 0.003	1.220 ± 0.003
$\langle l_1^2\rangle:\langle l_2^2\rangle:\langle l_3^2\rangle$				
RW[b]	1:(2.712 ± 0.029):(12.00 ± 0.14)	1:(2.540 ± 0.009):(6.334 ± 0.024)	1:(2.309 ± 0.008):(5.087 ± 0.020)	1:(2.140 ± 0.004):(4.338 ± 0.020)
Θ	1:(2.704 ± 0.009):(12.01 ± 0.11)	1:(2.492 ± 0.009):(6.148 ± 0.025)	1:(2.305 ± 0.012):(5.078 ± 0.017)	1:(2.147 ± 0.011):(4.351 ● 0.026)

[a] Random walk. [b] Random walk, Monte Carlo data.

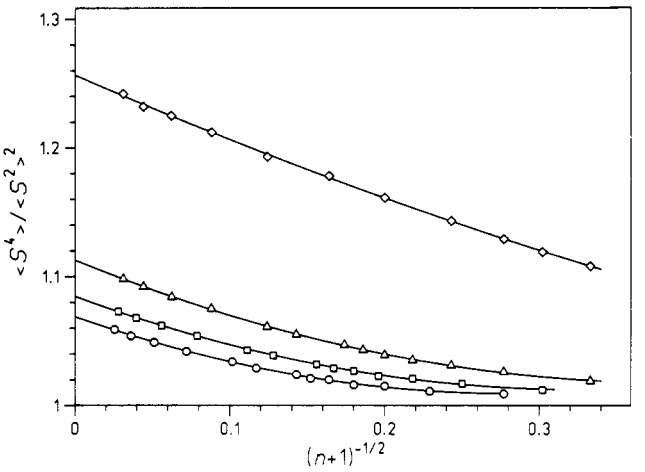

Figure 4. Dependence of the reduced moments of the distribution functions of the radius of gyration, $\delta_{4,2}^s$, on the number of segments for linear chains (-◇-) and stars with $f = 4$ (-△-), $f = 5$ (-□-), and $f = 6$ (-○-).

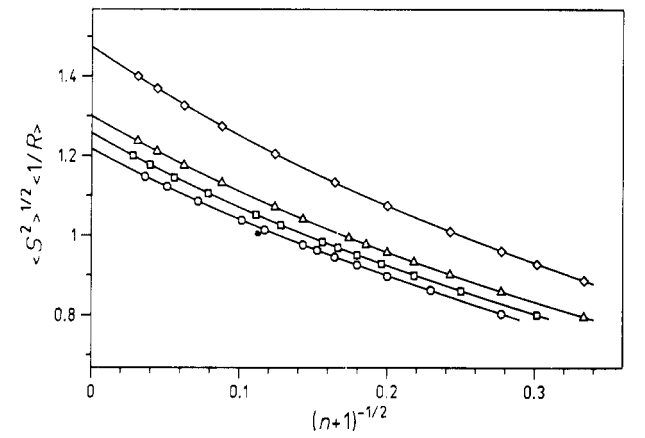

Figure 5. Dependence of the ratio $\langle S^2\rangle^{1/2}\langle 1/R\rangle$ on the number of segments. The symbols have the same meaning as those in Figure 4.

contrast to the determination of g, where the numerator and denominator of the ratio has been calculated for different models with different values of Φ_Θ (star and linear chain), the two quantities needed for the calculation of $\delta_{4,2}^s$ are always determined for the same model (either linear chain or star). Numerical errors arising from inaccuracies of Φ_Θ are mostly compensated in the latter case.

Guttman et al.[32] investigated the product $\langle S^2\rangle^{1/2}\langle 1/R\rangle$ for linear chains at the Θ point and obtained the asymptotic value 1.40. Their calculations are based on $\Phi_\Theta = 0.275$, which is not quite correct for reasons already discussed. The results of our calculations for linear and starlike

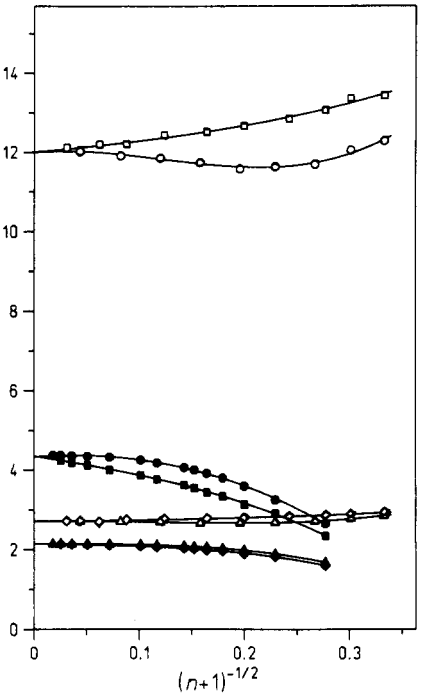

Figure 6. Dependence of the ratios of the principal axes of inertia on the number of segments for linear chains and stars with $f = 6$. The lower curves are plots of $\langle l_2^2\rangle/\langle l_1^2\rangle$ for Gaussian (-△-) and Θ-state molecules (-◇-); the upper curves fit the data of $\langle l_3^2\rangle/\langle l_1^2\rangle$ for Gaussian (-○-) and Θ-state linear chains (-□-). The corresponding symbols for the stars are filled.

molecules are illustrated in Figure 5. An F test showed that the fitting function (eq 1) had to be augmented by the term $d(n+1)^{-3/2}$. The asymptotic values can be found in Table I. The value for the linear chain differs somewhat from that (1.464) given earlier by W.B.[5] This arises from the extension of the calculations to longer chains ($n_{max} = 1024$ instead of $n_{max} = 128$ in the publication cited).

The last topic treated concerns the shape of the molecules represented by the principal axes of inertia. The n dependence of the ratios $\langle l_2^2\rangle/\langle l_1^2\rangle$ and $\langle l_3^2\rangle/\langle l_1^2\rangle$ is shown in Figure 6 for linear chains and stars ($f = 6$). Because of the lack of theoretical expressions, the data of the random-flight molecules have also been gained by Monte Carlo methods. Aside from the star with $f = 4$, not shown in the figure, the curves of the Gaussian and the Θ-state molecules run into nearly the same asymptotic value. The ratios for the random-flight molecules agree satisfactorily with those determined by other authors.[10,31] Corresponding data for molecules at the Θ state are missing in literature to our knowledge.

Conclusion

The asymptotic values of some ratios of static properties have been calculated for molecules in solution at the Θ state, defined by a vanishing second osmotic virial coefficient. They are always in the close vicinity of the corresponding Gaussian values. In some cases, however, these quantities are beyond the 95% confidence limits of the extrapolated data. It seems, therefore, to be an obvious conclusion that polymer molecules at the Θ state are non-Gaussian. On the other hand, one has to consider the fact that the extrapolations have been performed with empirical functions, which might be the source of some error. Whether polymer molecules at the Θ state are Gaussian or not is, therefore, still an open question.

A final remark may be in order, relating to the two methods of determination of the Θ temperature as discussed in the Introduction. If the data of $\langle S^2 \rangle_\Theta$ for $8 \leq n \leq 128$ are fitted to $\langle S^2 \rangle \propto n^{2\nu}$, a value of 1.0627 ± 0.0005 (1.0486 ± 0.0004) results for linear chains (stars with $f = 6$), whereas $2\nu = 1.028 \pm 0.001$ (0.994 ± 0.001) is obtained if $128 \leq n \leq 1536$. The values of 2ν for stars with $f = 4$ and 5 show a similar tendency. They decrease, if the range for which they were determined is shifted to larger values of n, and approach unity. This confirms once more the results of former work,[5,6] namely, that the asymptotic behavior of Θ molecules is approached much more slowly than that of the unperturbed ones. The last value (0.994) deviates considerably from unity. This can be attributed to the scattering of the data of stars with $f = 6$ already mentioned above. The extrapolation may, therefore, be somewhat uncertain.

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