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The Effect of Higher Order Interactions on Configurational Properties of Polymer Chains at the Θ State

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ABSTRACT: The configurational properties of polymer chains at the Θ state cannot be calculated exactly by two-parameter theories, because ternary (and higher order) interaction terms are still important. The size of the effect, which arises from the omission of these terms, was investigated. For this purpose, the characteristic ratios of simple chain models at the Θ state were evaluated by the RIS theory, which is based on two-parameter concepts, and by Monte Carlo methods at a state characterized by a vanishing second osmotic virial coefficient. The differences between the two results are considerable. On the other hand, the RIS theory has proved to be successful, when applied to more realistic models. The reasons for this apparent contradiction are discussed.

Introduction

When polymer molecules in dilute solution are treated by statistical mechanics, the complexity of the system is often reduced by considering the solvent as a continuum. The spatial configuration of a polymer molecule is thus governed by attractive and repulsive forces due to a potential of mean force, which depends on the temperature and the activity of the solvent. Through judicious selection of solvent and temperature, it is possible to obtain a state of the system at which attractive and repulsive forces are balanced and the solution behaves ideally in the thermodynamic sense. This means that the second osmotic virial coefficient vanishes. Flory defines this state as the Θ point of the polymer solution. It finds an exact parallel in the Boyle point of a real gas. Flory argues the following:[1–4] A state, where repulsion between a pair of chain units is exactly compensated by their mutual attraction, is equivalent to a state without any interaction involving pairs of units which are remote in the chain sequence. This means, a chain at the Θ point is equivalent to an unperturbed chain, the dimensions of which are influenced by short-range interferences solely.

The simplicity of Flory's concept allows model chains to be treated analytically in a straightforward manner, and many researchers have been inspired to develop corresponding formalisms. The results depend on the number of neighboring units considered to interact. The most refined model that has been treated up to now is the isomeric state model with interdependent rotation.[5–16] Flory devoted a comprehensive monograph to this topic.[4]

A quantitative description of the influence of intramolecular interactions on configurational and thermodynamic properties was first given by the two-parameter theory, the perturbation version of which can be sketched in its essential parts by

$$\langle h_n^2\rangle / \langle h_n^2\rangle_0 = 1 + \beta_2 f(\beta_2,n) \tag{1}$$

and

$$A_2(n) = n^2\beta_2 g(\beta_2,n) \tag{2}$$

$\langle h_n^2\rangle$ is the mean-square end-to-end distance of a chain with n bonds, β_2 is the binary cluster integral,

$$\beta_2 = \int \left\{1 - \exp\left[-\frac{w(\mathbf{r})}{kT}\right]\right\} \mathrm{d}\mathbf{r}$$

and A_2 is the second osmotic virial coefficient. The subscript 0 refers to a reference chain, generally a model chain with short interferences only, which resembles the essential features of the perturbed chain to be studied. If $A_2 = 0$, it follows from eq 2 that $\beta_2 = 0$ and therefore (eq 1) $\langle h^2\rangle_\Theta = \langle h^2\rangle_0$. This is in accordance with Flory's statements. The perturbation development given above, however, is incomplete. It does not include cluster integrals of higher order. (Flory[17] considered higher interaction terms in a theory on A_2, but he supposed their contribution to be small; so he neglected them in later work.) In most cases these terms are small compared with the binary interaction terms, and they can, therefore, be neglected. In the vicinity of the Θ temperature, however, the binary interaction terms assume values of the same order of magnitude as the higher interaction terms, so that the latter have also be taken into account.[18] The supplemented equations thus read

$$\langle h_n^2\rangle / \langle h_n^2\rangle_0 = 1 + \beta_2 f_2(\beta_2,n) + \beta_3 f_3(\beta_2,\beta_3,n) + \ldots$$

and

$$A_2(n) = \beta_2 g_2(\beta_2,n) + \beta_3 g_3(\beta_2,\beta_3,n) + \ldots$$

with the tertiary cluster integral

$$\beta_3 = \int \chi_{ij}\chi_{jk}\chi_{ik}\, \mathrm{d}\mathbf{r}_{ij}\, \mathrm{d}\mathbf{r}_{jk}$$

$$\chi_{\alpha\beta} = 1 - \exp\left[-\frac{w(\mathbf{r}_{\alpha\beta})}{kT}\right]$$

β_2 and β_3 do not vanish simultaneously at the same tem-

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perature. Therefore $A_2 = 0$ does not imply $\beta_2 = 0$ and $\langle h^2\rangle_\Theta = \langle h^2\rangle_0$; i.e., the mean-square end-to-end distance at the Θ temperature is different from that of the reference chain. This has been confirmed in two foregoing studies[19,20] and theoretically by Cherayil et al.[21,22]

On the other hand, numerous publications show that the rotational isomeric state (RIS) model, which rests upon the two-parameter theory, gives results in satisfactory accordance with experiment. The reasons for this contradictions are investigated in the following section.

Model and Equations

The investigation of the problem raised can hardly be made by a comparison of experimental data with the results of the RIS theory, since the former can be determined with a limited accuracy (5–15%) only, while the latter depends on a lot of parameters that are not all known exactly. Instead of it, simple well-defined models are used, which can be treated by both RIS theory and Monte Carlo "experiments". Suitable for this purpose are walks on a lattice, which meet the necessary requirements that bond lengths and bond angles are constant, and there exists a discrete set of rotational states.

Two models are used:

Model A. This model is a walk on a four-choice simple cubic lattice with the spacing l. The bond angle has the value $\pi/2$. The four rotational states are designated by trans (t; $\varphi_1 = 0$), gauche$^+$ (g$^+$; $\varphi_2 = \pi/2$), gauche$^-$ (g$^-$; $\varphi_3 = -\pi/2$), and cis (c; $\varphi = \pi$). The potential of mean force resulting from the superposition approximation is

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

and

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

Due to these definitions, intersections (two structural units of the chain occupy the same lattice site) are forbidden and each contact (two neighboring lattice sites are occupied by nonbonded units) contributes the amount of $-w$ to the total energy W. No additional potential is provided for the rotational states. Of course, the cis state has a lower potential ($-w$) because of the contact formed by the units j and $j + 3$.

Model B. This model is a walk on a diamond lattice with a bond angle of arccos (1/3) and three rotational states, trans ($\varphi_1 = 0$), gauche$^+$ ($\varphi_2 = 2\pi/3$), and gauche$^-$ ($\varphi_3 = -2\pi/3$). The potential of mean force is calculated by the method outlined for the first model.

The configuration of these models is studied at the Θ point, i.e., at the state of the vanishing second osmotic virial coefficient, A_2. As has been shown in ref 19, A_2 can be calculated by

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

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

The other 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.

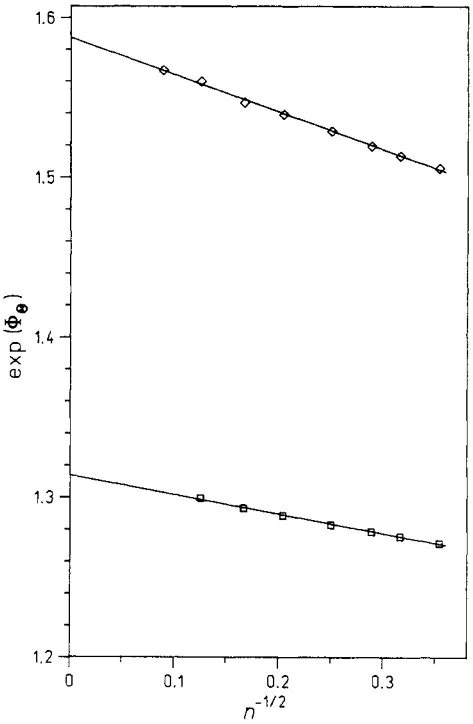

Figure 1. Plot of $\exp(\Phi_\Theta)$ versus $n^{-1/2}$ for chains on a four-choice simple cubic lattice (-□-) and on a diamond lattice (-◇-).

Now the value of βw has to be determined for which A_2 vanishes. In principle, this can be done analytically, but it would be a very time-consuming action for chains consisting of more than a few units. Therefore, instead of summing over the whole population of configurations, a Monte Carlo method was used.

Two nonintersecting chains with n bonds each were generated, and the number of intramolecular contacts were counted. The sum over the positions was calculated by shifting the two chains into each relative position to each other that gives rise to intermolecular contacts or intersections. Only these positions contribute to the sum. For the positions without any intersection, the number of intermolecular contacts was monitored. This procedure was repeated frequently for various values of $n \in \{8, 10, 12, 16, 24, 36, 64, (128)\}$. The sample sizes were 50 000 in each case. From the data thus generated, the value that nullifies A_2, Φ_Θ, can be found by variation of $\Phi \equiv \beta w$. The relative standard deviation of any Φ_Θ never exceeded 0.1%.

Because of the lack of a pertinent theory, a simple correlation between Φ_Θ and n was searched for by trial and error. An almost strict linearity for both models (with the correlation coefficients 0.9985 and 0.9988, respectively) was found by plotting $\exp(\Phi_\Theta)$ against $n^{-1/2}$ as shown in Figure 1. A similar behavior has been reported by Janssens and Bellemans[23] for chains on a five-choice simple cubic lattice. A likewise good linearity can be achieved if $(kT/w)_\Theta$ is plotted against $n^{-1/2}$.

The curves in Figure 1 were extrapolated to $n^{1/2} = 0$, since it seems to be improbable that they deviate significantly from linearity for higher values of n. The asymptotic values of $(kT/w)_\Theta$ thus obtained for model A are 3.662 ± 0.008 (3.635 ± 0.005) and for model B are 2.165 ± 0.003 (2.151 ± 0.003), where the data in parentheses result from the plot of $(kT/w)_\Theta$ against $n^{-1/2}$. Olaj and Pelinka,[24] using the condition $\langle h^2\rangle_\Theta \propto n$ to determine the Θ point, found 3.70 for the four-choice chain. In their comprehensive study of walks on the diamond lattice, Kremer et al.[25] obtained an asymptotic value of 2.25 ± 0.05 by considering the variation of the heat capacity and of the free energy with n. As can be seen, the differences between our data and those taken from literature are small, thus supporting the reliability of the calculations presented here.

On the basis of the potentials, Φ_Θ, the characteristic ratio of the end-to-end distance was calculated by a Monte Carlo technique of biased sampling.[26] The bond numbers considered were $n \in \{8, 10, 12, 16, 24, 36, 64, 128, 256, 512, 1024\}$ with sample sizes of 10^4 ($n = 8, 10$) up to 10^5. The estimated relative standard deviation amounted to 0.5% at most.

So far, chain models at the Θ state have been considered. The "experimental" data, which came out, shall be contrasted with the results of the RIS theory applied to the same models. According to this theory, the mean-square end-to-end distance can be evaluated by[27]

$$\langle h_n^2 \rangle / l^2 = 2Z^{-1}\mathbf{J}^*\mathbf{G}_1\mathbf{G}^{n-2}\mathbf{G}_n\mathbf{J}$$

The symbols have the following meaning: Z is the configuration partition function, given by

$$Z = \mathbf{j}^*\mathbf{U}^{n-2}\mathbf{j}$$

For model A, $\mathbf{j}^*$ and $\mathbf{J}^*$ are row vectors of order 1×4 and 1×20, respectively. They consist of an initial element of unity, with all other elements zero. The column vector $\mathbf{j}$ is four-dimensional with all elements equal to unity. $\mathbf{J}$ is a 20-dimensional column vector comprising 16 zeros followed by 4 elements equal to unity. $\mathbf{U}$ is the statistical weight matrix, in case of model A, given by

$$\mathbf{U} = \begin{array}{c} \\ (\mathrm{t}) \\ (\mathrm{g}^+) \\ (\mathrm{g}^-) \\ (\mathrm{c}) \end{array} \begin{array}{c} \begin{array}{cccc} (\mathrm{t}) & (\mathrm{g}^+) & (\mathrm{g}^-) & (\mathrm{c}) \end{array} \\ \begin{pmatrix} 1 & 1 & 1 & \sigma \\ 1 & 1 & 1 & \sigma \\ 1 & 1 & 1 & \sigma \\ 1 & 1 & 1 & 0 \end{pmatrix} \end{array}$$

The statistical weights have been calculated on the basis of the set of energies given by the features of the model. With the element $\sigma \equiv \exp(\Phi_\Theta)$, the contact of the cis conformation is allowed for. The interactions that depend jointly upon two consecutive angles are equal to zero, except they are both in the cis state. This conformation gives rise to an intersection, and this means that the statistical weight equals zero.

The generator matrix is of the order 20×20 and defined by

$$\mathbf{G} = \begin{pmatrix} \mathbf{U} & (\mathbf{U} \otimes \mathbf{m}^{\mathrm{T}})\|\mathbf{T}\| & (1/2)\mathbf{U} \\ 0 & (\mathbf{U} \otimes \mathbf{E}_3)\|\mathbf{T}\| & \mathbf{U} \otimes \mathbf{m} \\ 0 & 0 & \mathbf{U} \end{pmatrix}$$

$\mathbf{m}$ is a three-dimensional unit vector pointing along the x axis. $\mathbf{E}_3$ has the usual meaning of a three-dimensional unit matrix. $\|\mathbf{T}\|$ is a pseudodiagonal matrix of order 12×12 obtained by placing the $\mathbf{T}$ matrices for the four rotational states of a bond in diagonal array. The transformation matrix $\mathbf{T}$ is

$$\mathbf{T}_i = \begin{pmatrix} \cos\vartheta & \sin\vartheta & 0 \\ \sin\vartheta\cos\varphi_i & -\cos\vartheta\cos\varphi_i & \sin\varphi_i \\ \sin\vartheta\sin\varphi_i & -\cos\vartheta\sin\varphi_i & -\cos\varphi_i \end{pmatrix}$$

For model A, this assumes the forms

$$\mathbf{T}_1 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \mathbf{T}_2 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\mathbf{T}_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix} \quad \mathbf{T}_4 = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

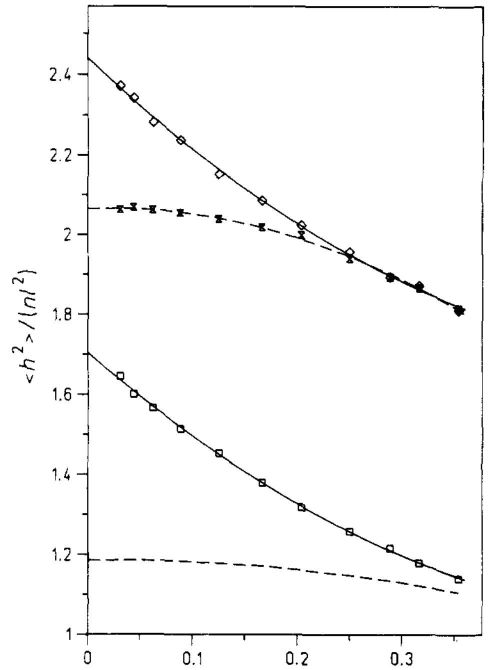

Figure 2. Dependence of the characteristic ratio on the number of bonds calculated at the Θ state and by means of the RIS theory (dashed curves). (–▶◀–) RIS chains on the diamond lattice; the other symbols have the same meaning as in Figure 1.

respectively. The terminal matrices $\mathbf{G}_1$ and $\mathbf{G}_n$ are constructed similar to $\mathbf{G}$ with $\mathbf{E}_4$ replacing $\mathbf{U}$. By means of this formalism, the characteristic ratio $\langle h_n^2 \rangle / (nl^2)$ was calculated for several values of n.

The treatment of chains on the diamond lattice is somewhat cumbersome, because it requires the setting up of matrices with 125×125 elements. Therefore, the calculations were performed by a Monte Carlo method. The calculations for chains on a diamond lattice described in a preceding paragraph were repeated with some modifications: Only structures with rings of six bonds were precluded, and only contacts between the structural units j and $j + 5$ were counted. This is an adequate transformation of the ideas of the RIS theory, as can easily be seen.

Results and Discussion

All the characteristic ratios, C_n, calculated in the preceding section are shown in Figure 2, where they are plotted against $n^{-1/2}$. There is no theoretical justification for this procedure, but the data points of the Θ chains can be fitted smoothly by a second-order polynomial in $n^{-1/2}$, with correlation coefficients ≈ 0.999. The lower pair of curves represent the values of model A, the upper pair those of model B. The values predicted by the RIS theory are plotted by dashed curves.

As can be found by simple considerations, the Θ chain and the RIS chain are identical for small values of n (<5 for model A, <7 for model B). The corresponding parts of the curves are not shown in Figure 2, but the behavior of the curves in this range can easily be deduced from their courses. For values of n beyond, say, 50, the characteristic ratios of the Θ chain and the RIS chain no longer agree. Moreover, the RIS chains attain substantially the asymptotic values of the characteristic ratio if they are longer than 100 bonds, whereas the asymptotic behavior of the Θ chains is approached only very slowly. The differences between the C_∞ (Θ) and C_∞ (RIS) relative to C_∞ (RIS) amount to $\approx$40% (A) and $\approx$20% (B).

These results obtained on well-defined model chains are in accordance with the considerations in the Introduction. They exhibit that the dimensions of Θ chains cannot be evaluated exactly by the RIS theory.

Frequently a definition of the Θ temperature is found in the literature that is different from that used in this paper and that has the form

$$\Theta = \lim_{n \to \infty} T(A_2{=}0)$$

Strictly speaking, this definition is unsuited for an exact description of thermodynamical properties, which depend, of course, on the second osmotic virial coefficient of the respective member of the homologous series considered. But it can be shown that this is a point of minor importance: Φ_Θ is a monotonically increasing function of n; i.e., an increasing attractive potential is necessary to keep $A_2 = 0$. The characteristic ratios of short chains, subjected to Φ_Θ of the infinite chain instead of the correct Φ_Θ, become smaller, the effect being larger as n lowers. This is valid for both models and both calculation modes. Test calculations proved moreover that such small changes in Φ had only a weak influence on the characteristic ratio (<1%). This means that the bad agreement of the characteristic ratios cannot be traced back to the different definitions of the Θ temperature.

Now let us return to the question to the success of the RIS theory, when applied to more complex real molecules. A significant reason lies surely in the fact that the interactions, which are considered to be long ranged (to speak in terms of the two-parameter theory) and which are, therefore, neglected in the various RIS calculations, differ widely. In our models, the contacts that might be formed by structure units j and $j + 5$ (A) (or $j + 7$ (B)) as well as the possible ring closure between structure units j and $j + 6$ (A) (or $j + 7$ (B)) are ignored. In a polyethylene-like chain, the H atoms attached to the backbone have to be taken into account, with the effect that the potential minima are shifted to larger distances from the C atoms. This leads to a soft repulsion between the structure units j and $j + 3$ in the gauche conformation and a strong repulsion between the structure units j and $j + 4$ in the configuration $g^{\pm}g^{\mp}$ (pentane effect). The next configurations, which give rise to interferences but which are neglected by the RIS theory, are $g^{\pm}g^{\pm}tg^{\pm}g^{\pm}tg^{\pm}g^{\pm}$. This "undecane" effect, comparable with the pentane effect, is, however, of much longer range than the encounters ignored in models A and B, and, therefore, statistically more improbable. As has already been noted, the relative difference $(\langle h^2\rangle_\Theta - \langle h^2\rangle_0)/\langle h^2\rangle_0$ is less for model B as against model A. For the reasons discussed above, it can be expected to be even smaller, if the models are closer to real molecules. Therefore, it is possible that the difference between the results of the RIS theory and experiment cannot be detected, because it is hidden in the error bar.

An additional remark may be in order: It is not possible to extract the n dependence of the Θ temperature from Φ_Θ, since—as already has been mentioned—w is a potential of mean force and, therefore, a function of the temperature and of the activity of the solvent particles surrounding the polymer chains. The influence of these quantities on w may easily be studied by recalling a universal feature of polymer solutions, namely, the existence of a lower (L) and of an upper (U) critical solution temperature,[28] in the vicinity of which A_2 vanishes. This means that there are also two Θ temperatures, Θ_L and Θ_U. On the other hand, Monte Carlo calculations prove A_2 to be a monotonically decreasing functional of Φ.[23] The equation $A_2 = 0$ has, therefore, only one solution so that $\Phi_{\Theta_U} = \Phi_{\Theta_L}$ even though $\Theta_U \neq \Theta_L$.

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