The Third Osmotic Virial Coefficient of Polymer Solutions

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ABSTRACT: The third osmotic virial coefficient, A_3, of chain molecules confined to simple cubic, face-centered cubic, and diamond lattices was determined by Monte Carlo methods. The data of each model appear to follow the same power law with an exponent in accordance with scaling predictions. The ratio $A_3/(nA_2^2)$ for long chains turns out to be universal and is near 0.30.

Introduction

In a recent publication[1] the dependence of the second osmotic virial coefficient (A_2) of polymer molecules in solution on their chain length was investigated by Monte Carlo calculations for nonintersecting near-neighbor walks on various three-dimensional lattices. The values obtained obey a similar power law as has been found experimentally, and the exponent is in perfect accordance with scaling predictions. It is, therefore, of interest to extend the investigations to the third osmotic virial coefficient (A_3) to study its scaling behavior. Only a few publications report relevant experimental data, because it is difficult to extract the influence of A_3 from the deviation from van't Hoff's law which is generally dominated by the term with A_2.

From the theoretical viewpoint all the virial coefficients can be explained[2] as functionals of the potential of mean force. But even when the potential is known, the exact evaluation of the virial coefficients of long flexible molecules resists all mathematical efforts, so that only perturbation expansions and expressions based on simplifying assumptions[3] have been developed. De Gennes[4] was one of the first to attack problems of polymer physics by the intuitive method of scaling analysis. This method has been successful in many respects. One is therefore encouraged to extend the arguments leading to the power law of A_2, to a corresponding expression for A_3. We do so in this paper, treating in order the following subjects: (i) derivation of a power law for A_3, (ii) description of the lattice models and related Monte Carlo algorithms, and (iii) calculation of the ratio $A_3/(nA_2^2)$ and comparison with experimental results and with the predictions of renormalization group theory.

Basic Equations and Model

The virial expansion of the osmotic pressure, Π, of a polymer in solution is given by

$$\beta\Pi = \frac{c}{n} + A_2c^2 + A_3c^3 + ... \qquad (1)$$

β has the usual meaning $1/(kT)$. n is the number of structural units comprising a chain, and c is the concentration of the units. According to the scaling hypothesis[4] the osmotic pressure can be expressed by

$$\beta\Pi = \frac{c}{n}F\left(\frac{c}{c^*}\right) \qquad (2)$$

The scaling variable c^* is defined as that concentration at which the polymer coils start to overlap each other, i.e., $c^* \propto n/\langle S^2\rangle^{3/2} \propto n^{1-3\nu}$. $\langle S^2\rangle$ is the mean-square radius of gyration and ν the scaling exponent (=0.588[5,6]). For $c < c^*$ the appropriate representation of the function F is a power series in c/c^* so that

$$\beta\Pi = \frac{c}{n}\left[1 + a_2\left(\frac{c}{c^*}\right) + a_3\left(\frac{c}{c^*}\right)^2 + ...\right] \qquad (3)$$

A comparison of the coefficient of c^3 in this equation with the corresponding one of eq 1 leads to

$$A_3 = \frac{a_3}{nc^{*2}} \propto n^{6\nu-3} = n^{0.528} \qquad (4)$$

As can be seen there is a fundamental difference between the behavior of the two virial coefficients: while A_2 vanishes asymptotically with increasing n, A_3 is divergent.

With a slight modification of the nomenclature found in Yamakawa's book,[3] A_3 can be expressed in the following form:

$$A_3 = 4nA_2^2 - \frac{1}{3Vn^3}\int[F_3(1,2,3) - F_1(1)F_2(2,3) - F_1(2)F_2(1,3) - F_1(3)F_2(1,2) + 2F_1(1)F_1(2)F_1(3)]\,\mathrm{d}(1,2,3) \qquad (5)$$

and similarly

$$A_2 = \frac{1}{2Vn^2}\int[F_1(1)F_1(2) - F_2(1,2)]\,\mathrm{d}(1,2) \qquad (6)$$

with

$$F_1(1) = \exp[-\beta W_1(1)]$$

$$F_2(1,2) = \exp[-\beta W_2(1,2)] \qquad (7)$$

$$F_3(1,2,3) = \exp[-\beta W_3(1,2,3)]$$

These equations define the potential of mean force, $W_j(1, 2, ..., j)$, of a system consisting of j molecules. Their coordinates are represented by $(1, 2, ..., j)$. The right-hand side of the equations can be reduced using a decomposition of the potential of mean force into a sum of terms with intramolecular and intermolecular potentials, as $W_3(1,2,3) = W_1(1) + W_1(2) + W_1(3) + W_{12} + W_{13} + W_{23}$, so that

$$F_2(1,2) = F_1(1)F_1(2)\,\mathrm{e}^{-\beta W_{12}}$$

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$$F_3(1,2,3) = F_1(1)F_1(2)F_1(3)\, e^{-\beta(W_{12}+W_{13}+W_{23})}$$

The potentials are assumed to be computable by addition of the pair potentials of the structural units (superposition approximation), i.e., $W_1(1) = \Sigma_{i<j} w(1_i,1_j)$ or $W_{12} = \Sigma_{i,j} w(1_i,2_j)$. The symbol 1_i resembles the coordinates of the ith structural unit of molecule 1. Three-body interactions are neglected, and indeed they do not arise in the hard-core potentials to be considered in the simulation. The potential W_1 thus calculated is, however, not identical to that required in eq 7, because it generally does not satisfy the normalization condition of the McMillan-Mayer theory:

$$\int F_1(j)\, d(j) = V$$

To obtain a proper form, the zero of the model potential has to be shifted. The way this can be done is to set

$$F_1(j) = \frac{\exp[-\beta W_1(j)]}{\int \exp[-\beta W_1(j)]\, d(j)_{int}} \tag{8}$$

where the integration extends over the internal degrees of freedom. As can easily be verified, the normalization condition is satisfied now. In contrast to eq 7 the symbol W_1 has now the meaning of the potential applied. It differs from the potential in eq 7 by a constant. From eq 8 follows that $F_1(j)/V\, d(j)$ is the probability to observe a configuration of molecule j in the vicinity of the coordinate set (j).

Equation 6 can now be written

$$A_2 = \frac{1}{2Vn^2}\int F_1(1)F_1(2)(1 - e^{-\beta W_{12}})\, d(1,2) \tag{9}$$

and the integrals can be separated

$$A_2 = \frac{1}{2Vn^2}\int F_1(1)F_1(2)\, d(1)\, d(2)_{int}\int (1 - e^{-\beta W_{12}})\, d\mathbf{R}_{12}$$
$$= \frac{1}{2V^2n^2}\int F_1(1)F_1(2)\, d(1,2)\int (1 - e^{-\beta W_{12}})\, d\mathbf{R}_{12}$$

$\mathbf{R}_{12}$ is the vector connecting the first structural units of the two chains. Recalling the definition of $F_1(j)$, one obtains

$$A_2 = \frac{\langle f_{12}\rangle}{2n^2} \tag{10}$$

where

$$f_{12} = \int (1 - e^{-\beta W_{12}})\, d\mathbf{R}_{12} \tag{11}$$

So $\langle f_{12}\rangle$ may be identified as the canonical ensemble average of f_{12} taken with the energies $W_1(1) + W_1(2)$, i.e., the sum of the intramolecular potentials of mean force.

Similar considerations can be applied to A_3. Starting with eq 5 one obtains

$$A_3 = \frac{\langle f_{12}\rangle^2}{n^3} - \frac{1}{3Vn^3}\int F_1(1)F_1(2)F_1(3)[e^{-\beta(W_{12}+W_{13}+W_{23})} - e^{-\beta W_{12}} - e^{-\beta W_{13}} - e^{-\beta W_{23}} + 2]\, d(1,2,3)$$
$$= \frac{\langle f_{12}\rangle^2}{n^3} - \frac{1}{3Vn^3}\int F_1(1)F_1(2)F_1(3)[(1 - e^{-\beta W_{12}})(1 - e^{-\beta W_{13}})(1 - e^{-\beta W_{23}}) - (1 - e^{-\beta W_{12}})(1 - e^{-\beta W_{13}}) - (1 - e^{-\beta W_{12}})(1 - e^{-\beta W_{23}}) - (1 - e^{-\beta W_{13}})(1 - e^{-\beta W_{23}})]\, d(1,2,3)$$
$$= \frac{\langle f_{12}\rangle^2}{n^3} + \frac{1}{3n^3}(\langle f_{12}f_{13}f_{23}\rangle - \langle f_{12}f_{13}\rangle - \langle f_{12}f_{23}\rangle - \langle f_{13}f_{23}\rangle)$$

with the final result

$$A_3 = \frac{1}{3n^3}(\langle g_{123}\rangle - \langle f_{12}f_{13}\rangle - \langle f_{12}f_{23}\rangle - \langle f_{13}f_{23}\rangle + \langle f_{12}\rangle\langle f_{13}\rangle + \langle f_{12}\rangle\langle f_{23}\rangle + \langle f_{13}\rangle\langle f_{23}\rangle) \tag{12}$$

The meaning of the products like $f_{12}f_{13}$ can easily be deduced from eq 11, while g_{123} is defined by

$$g_{123} = \int (1 - e^{-\beta W_{12}})(1 - e^{-\beta W_{13}})(1 - e^{-\beta W_{23}})\, d\mathbf{R}_{12}\, d\mathbf{R}_{13} \tag{13}$$

The polymer molecules were simulated by nonintersecting near-neighbor random walks on various three-dimensional lattices, namely simple cubic (SC), face-centered cubic (FCC), and diamond (D). Each molecule consists of n structural units placed on neighboring lattice sites at a distance l from each other. There are no interactions apart from these hard-core potentials so that the solution is athermal, and only self-avoiding configurations [$W_1(j) = 0$ and $F_1(j) = 1$] contribute to the averages. It may be shown that $\langle f_{12}f_{13}\rangle = \langle f_{12}\rangle\langle f_{13}\rangle$ for hard-core systems. Similar relations hold for the other averages so that

$$A_3 = \frac{\langle g_{123}\rangle}{3n^3} \tag{14}$$

The integral in eq 13 can be easily performed with the result

$$g_{123} = v^2 \sum_{\mathbf{R}_{12}}\sum_{\mathbf{R}_{13}} (1 - e^{-\beta W_{12}})(1 - e^{-\beta W_{13}})(1 - e^{-\beta W_{23}}) \tag{15}$$

where v is the volume of one lattice site (identical to the volume of one structural unit). The summations extend over all possible vectors $\mathbf{R}_{ij}$ with integer components. Relevant, however, are only those vectors that cause the three chains to intersect pairwise. Otherwise at least 1 of the 3 factors of eq 13 enclosed in parentheses would vanish. Thus the double sum counts the number of positions of three chains with given configurations at which pairwise intersections occur, the position of say chain 1 being fixed. This means

$$\frac{A_3}{v^2} = \frac{1}{3n^3}\left\langle \sum\nolimits'_{\mathbf{R}_{12}} \sum\nolimits'_{\mathbf{R}_{13}} 1 \right\rangle \tag{16}$$

The primes on the summation symbols indicate that the summation is restricted to the rules set up above.

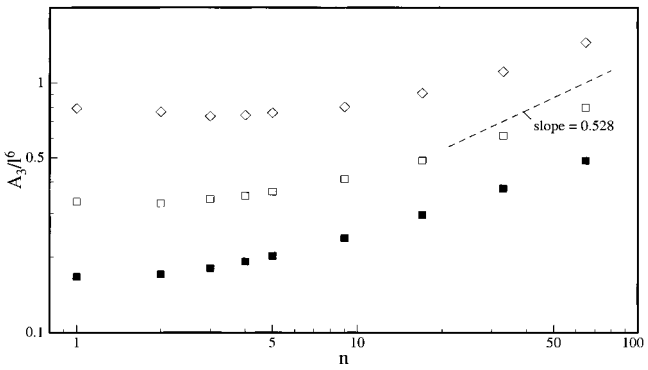

Figure 1. Dependence of the reduced third osmotic virial coefficient (A_3/l^6) on the number of structural units (n) for chains on simple cubic (□), face-centered cubic (■), and diamond (◇) lattices.

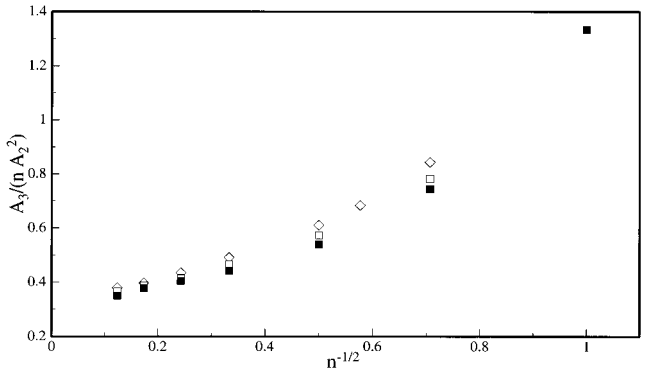

Figure 2. Dependence of the ratio A_3/nA_2^2) on the number of structural units n in the polymer chain. The meaning of the symbols is found in the caption of Figure 1.

In this work the ensemble average of eq 16 was estimated by calculating the average of a Monte Carlo sample. For this purpose three chains of the intended length (n) were randomly generated. While the position of chain 1 was always kept fixed, chain 2 was shifted to each position where an intersection with chain 1 is possible. The n^2 shift vectors $\mathbf{R}_{12}$ were stored in one computer word each and sorted.[7] This sorting facilitates the search for identical vectors which appear if the chains intersect more than once in a one-cluster configuration. Only one of these vectors was kept in storage, which now contained n_{12} different vectors. The n_{13} vectors of the kind $\mathbf{R}_{13}$ were obtained by application of the same method to the chains 1 and 3. Subsequently each of the $n_{12}n_{13}$ possible combinations of the shift vectors were tested to see whether chain 2 intersected chain 3 at least once. The total number of these combinations is equal to g_{123}. This procedure was then repeated to generate a sample of an appropriate size. The sample mean of g_{123} is the quantity $\langle g_{123}\rangle$ required for eq 14.

The number of structural units of the chains investigated were $n \in \{3,4,5,9,17,33,65\}$ with sample sizes of 10 000 (for $n = 65$ only 100).

Results and Discussion

Figure 1 shows a double-logarithmic plot of the reduced virial coefficient versus n for all lattices investigated. The relative standard deviations are about 10% for $n = 65$ and 1% in all other cases. A_3 is reduced by l^6 instead of v^2. This has been done because v depends on the kind of lattice, whereas l is a property common to all chains. The conversion $v = cl^3$ was performed by means of the factors $c = 1$ (SC), $c = 1/2^{1/2}$ (FCC), and $c = 8/3^{3/2}$ (D).

As can be seen the data points in the range investigated do not follow a straight line. The chains are too short for a study of their asymptotic behavior. Nothing else was really to be expected. For comparision: the data for A_2[1] became linear with the slope theoretically predicted only for $n > 1000$. The data points in Figure 1 are consistent with the conjecture that a slope of 0.528 (as indicated by the line in the figure) will be attained for all three models at large n. Corroboration requires the generation of much longer chains which is not feasible at present because of the excessive amount of computing time required. Some experimental determinations of this exponent have been made using light-scattering measurements. From their data Kniewske and Kulicke[8] proposed a power law for A_2. Using the relation $A_3 = gnA_2^2$ already suggested by Flory[9] (with $g = 1/3$) they were enabled to evaluate the corresponding power law for A_3. The result of this indirect method was 0.58. Nakamura et al.[10] analyzed their data using a direct procedure and obtained an exponent of 0.6.

An interesting quantity is the ratio $g = A_3/(nA_2^2)$. According to the two-parameter theories[3] g should be a function of n, whereas renormalization group theories predict that g is a universal constant. The experimental results are not sufficient to decide between the two possibilities. Kniewske and Kulicke established that their data agree with Flory's relation, while Nakamura et al. found an increasing g with increasing n. Oettinger[11] investigated many-chain systems on a simple cubic lattice using Monte Carlo methods. He found values for g between 0.56 (7) and 0.41 (30), depending on the respective chain length given in parentheses. The result from renormalization group calculations[12] is $g = 0.277$. The values of A_2 taken from our earlier work[1] and those for A_3 from this study allow us to evaluate the universality of g and its asymptotic limit. This is shown in Figure 2, where g is plotted against $n^{-1/2}$. The following features can be noticed: (i) the data do not indicate any dependence on the kind of lattice, when n is sufficiently large and (ii) the asymptotic value is in the vicinity of 0.30, as can be found by the extrapolation of the line through the three left-most points of each data set. These results support the predictions of the renormalization group theory with respect to the universality of g, but not with respect to its size.

References and Notes

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