The Second Osmotic Virial Coefficient of Polymer Solutions

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ABSTRACT: The second osmotic virial coefficient, A_2, of chain molecules confined to SC, FCC, and diamond lattices was determined by Monte Carlo methods. In each case the dependence of A_2 on the chain length follows a power law with nearly identical exponents, which are in accordance with the scaling predictions. A fair agreement with the results of other authors for models in the continuous space indicates a universal behavior.

Introduction

The second osmotic virial coefficient, A_2, is a many-sided indicator of thermodynamic as well as configurational and transport properties of dilute polymer solutions. It is defined via the virial expansion of the osmotic pressure, Π, the number of structural units comprising a chain, n, and their concentration, c, as

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

β has the usual meaning, $1/(kT)$. Some features of A_2, well-known to each polymer chemist, are as follows: the greater A_2,

−the greater the deviation of the solution from ideal behavior, described by van't Hoff's law,

−the stronger the interaction between solute and solvent molecules (the "better" the solvent),

−the stronger the swelling of the polymer coils,

−the higher the viscosity of the solution.

The first attempts to interprete the properties of A_2 in terms of the properties and interactions of the constituent solvent and polymer molecules were made by Flory[1] and Huggins by means of a lattice model with a mean field approximation. This theory predicts A_2 to be independent of n. This, however, is in contradiction to experimental results, which show that A_2 is a decreasing function of n. As early as the 50's this dependence was thought to take the form of a power law, $A_2 \propto n^{-\gamma}$ with $\gamma > 0$. The exponent γ was considered to be an adjustable parameter with values around 0.23,[2] although values of 0.38[3] and 0.15[4,5] were also reported. McMillan and Mayer[6] developed a theory by which A_2 can be described in terms of molecular parameters. Treating this expression with the perturbation method, Yamakawa[7] and others found a theoretical explanation for the n-dependence of A_2 in the form of a series. Most of the approximate theories available at that time predicted that the series converges and that A_2 is proportional to $\langle S^2\rangle^{3/2}/M^2$, where $\langle S^2\rangle$ is the mean-square radius of gyration and M is the molecular weight.

Later on this result was further supported by scaling concepts.[10] In the case of dilute polymer solutions the appropriate scaling function is a power expansion of the osmotic pressure with respect to c. To make the argument dimensionless, c is scaled by c^*, which is defined as that concentration at which the polymer coils start to overlap each other, i.e. $c^* \propto n/\langle S^2\rangle^{3/2} \propto n^{1-3\nu}$ with the scaling exponent $\nu = 0.588$.[8,9] A brief repetition of the arguments, originally set forth by de Gennes,[10] shows that

$$\beta\Pi = \frac{c}{n}F\left(\frac{c}{c^*}\right) \rightarrow \frac{c}{n}\left(1 + a_2\frac{c}{c^*} + ...\right) \qquad (2)$$

a_2 is a numerical factor that does not depend on c. The comparison of the corresponding coefficients of c with those of eq 1 leads to

$$A_2 = \frac{a_2}{nc^*} \propto n^{3\nu-2} \qquad (3)$$

Thus the exponent γ can be supposed to be around $^1/_5$.

There have been several attempts to evaluate γ by simulation methods on chain models that are both continuous and on-lattice. The range of values found extends from 0.25[11] over 0.272,[12] 0.278,[13] and 0.28[14] to 0.33.[15] Compared with the scaling predictions, all these values are too large. Several reasons may be responsible for these deviations and for the differences between the values of γ:

i. the chains, investigated by simulation, were too short;

ii. the algorithms used generated samples with a poor statistics;

iii. γ is not a constant but depends on the kind of model.

The last reason requires some comment. Numerous investigations have proven that the principle of universality holds for single chains irrespective of their modeling. From this, however, it cannot be concluded that the same is true for a system of two chains. A_2 is evaluated by averaging a functional of the intermolecular interactions over all possible configurations. The main contribution for the value of the functional arises from positions where the two chains are close neighbors. If the chains are modeled as a walk on a lattice, the number of these positions is small compared to those for off-lattice chains, in which case it goes to infinity. This might affect γ, at least for short chains.

The aim of this paper is to clarify these points.

Basic Equations and Model

Since the values of A_2 shall be estimated by Monte Carlo simulations on lattices, the appropriate equation, derived from the corresponding expression of the McMillan−Mayer theory,[6] is

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$$\frac{A_2}{v} = \frac{\sum_i \sum_j \exp\{-\beta[W_1(i) + W_1(j)]\} \sum_p \{1 - \exp[-\beta W_{12}(p|i,j)]\}}{2(n+1)^2 \sum_i \sum_j \exp\{-\beta[W_1(i) + W_1(j)]\}} \tag{4}$$

The symbols have the following meanings: v characterizes the volume of one lattice site. $W_1(i)$ and $W_1(j)$ are the intramolecular potentials of mean force of two molecules, when they are in the configuration states i and j, respectively. $W_{12}(p|i, j)$ is the intermolecular potential of mean force between the two molecules, when they are in relative position p, given the respective states i and j. p may be considered as the vector joining the first structural units of the two chains or any other quantity, by which their relative positions can be described. The summations extend over all possible configurations (i, j) and relative positions (p) of the two molecules. Thus A_2/v can be interpreted as the canonical ensemble average of the sum $\sum_p\{1 - \exp[-\beta W_{12}(p)]\}$, corresponding to Mayer's f-function, taken with energetics $W_1(i) + W_1(j)$, i.e. the sum of the intramolecular potentials of mean force,

$$\frac{A_2}{v} = \frac{\langle \sum_p \{1 - \exp[-\beta W_{12}(p)]\} \rangle}{2(n+1)^2} \tag{5}$$

The polymer molecules were simulated by nonintersecting walks on various three-dimensional lattices [simple cubic (SC), face-centered cubic (FCC), and diamond (D)]. They consist of n steps (bonds) of length l (lattice spacing) each and occupy, therefore, $n + 1$ lattice sites. There are no interactions apart from these hard-core potentials so that the solution is athermal, and only self-avoiding configurations ($W_1 = 0$) contribute to the sums over i and j. Concerning the summation over p only those relative positions are relevant at which the two chains intersect each other. In this case the term of eq 5 enclosed in braces becomes unity, otherwise it vanishes. Thus eq 5 simplifies to

$$\frac{A_2}{v} = \frac{1}{2(n+1)^2} \langle \sum\nolimits'_p 1 \rangle \tag{6}$$

where the prime indicates the restriction in the summation. The sum is, therefore, identical to the number of relative positions of the two chains at which one intersection occurs at least.

In this work the averaging process was not performed over the whole population of configurations, but only over a randomly generated sample of up to 10 000 chain pairs. The sum over p, however, was not estimated by a Monte Carlo method but calculated exactly, because tests have shown that the estimate of A_2 depends highly on a correct evaluation of this sum, whereas the sample size is less critical.

For the estimation of A_2 of short chains with $n \in \{2, 4, 8, 16, 32, 64\}$ a sample of chain pairs was generated by simple sampling. Thus the members of the sample are independent of each other. For longer chains, however, this method is known to suffer from severe attrition. For this reason the pivot algorithm[16,17] was employed for chains with $n \in \{128, 256, 512, 1024\}$. Since the summation over p is the most time-consuming process and succeeding chain configurations, generated in this way, are correlated, the sum was not evaluated at every step of the simulation run but at every $t_{1/e}$th step, to ensure a sufficient statistical independence of the data. $t_{1/e}$ was estimated in preliminary runs from the correlation function of the radius of gyration

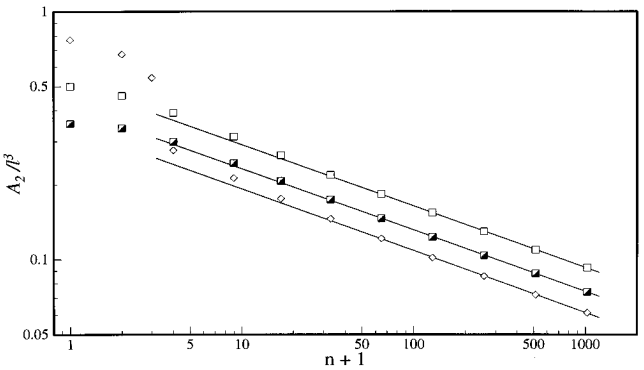

Figure 1. Dependence of the reduced second osmotic virial coefficient (A_2/l^3) on the number of structural units ($n + 1$) for chains on simple cubic (□), face centered cubic (◪), and diamond (◇) lattices.

$$C(S^2,t) = \frac{\langle S^2(0)S^2(t)\rangle - \langle S^2\rangle^2}{\langle S^4\rangle - \langle S^2\rangle^2} \tag{7}$$

since $C(S^2,t)$ can be considered as a measure for the configurational relaxation on the Monte Carlo trajectory. t counts the number of simulation steps. The value of t, at which $C(S^2,t)$ has decayed to $1/e$, was assumed to be an appropriate interval. It turned out to be about 10, nearly independent of the chain length.

To calculate the sum in eq 6, one of the two chains was shifted to each position where an intersection happens; the other chain remained fixed in space. There are $(n + 1)^2$ possible movements, characterized by the vectors $\mathbf{r}_{i_1} - \mathbf{r}_{j_2}$ with $i_1, j_2 \in \{0, 1, ..., n\}$. $\mathbf{r}_{k_\alpha}$ is the position of the kth structural unit of the αth chain. The shift vectors were stored in one computer word each and sorted.[18] In the case of a k-fold intersection k shift vectors are identical. Of course they have to be counted only once. The sorting facilitates the search for them. The number of different vectors found is identical with the sum in eq 6.

Results and Discussion

For a "chain" consisting of one structure unit ($n = 0$), A_2/v is 0.5, as can be seen by simple considerations with the help of eq 6. Chain pairs with $n \geq 1$ can intersect more than once, and for this reason A_2/v decreases continuously with increasing n. These contemplative findings are confirmed by the results of the simulation. Figure 1 shows a double-logarithmic plot of the reduced virial coefficient versus the number of structure units for all lattices investigated. The relative standard deviations never exceeded 0.2%. For this reason error bars are not drawn, since they would always be smaller than the symbols used to characterize the data points. In the figure A_2 is reduced by the bond length cubed, l^3, instead of by the volume of a lattice site, v. This facilitates the comparison of the data, because v depends on the kind of lattice, whereas l is a property common to all chains. The conversion $v = cl^3$ was performed

using the factors $c = 1$ (SC), $c = 1/\sqrt{2}$ (FCC), and $c = 8/(3\sqrt{3})$ (D).

For $n \geq 64$ the data seem to exhibit strictly linear behavior. The slopes, found by regression analysis, are nearly equal, with 0.248 (SC), 0.247 (FCC), and 0.249 (D). These results are in good agreement with the findings of Yethiraj et al.[11] for continuous space hard chains, published most recently. They deviate, however, somewhat from the scaling prediction $\gamma = 2 - 3\nu = 0.236$. Since it may be possible that the values of n in the range considered are still too small, the same data sets as above were fitted by second-order polynomials, complemented by F tests.[19] It turned out in each case that the fit with a quadratic polynomial improves significantly the fit over the linear functions and that the curvature is positive. This suggests the conclusion that the dependence of $\ln A_2/l^3$ on n does not exhibit a linear behavior within the range considered and that the value of γ has been overestimated. Indeed, the slopes of the lines connecting the data points with $n = 512$ and 1024 have values of 0.239, 0.249, and 0.239, respectively, which are partly in the vicinity of the theoretically predicted 0.236.

To sum up, it can be established that the results presented together with those of other authors confirm the universal character of γ. Moreover there are strong indications that in the asymptotic limit its value agrees with the scaling predictions.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(2) Outer, P.; Carr, C. I.; Zimm, B. H. *J. Chem. Phys.* **1950**, *18*, 830.
(3) Schulz, G. V.; Meyerhoff, G. *Z. Elektrochem.* **1952**, *56*, 545.
(4) Bawn, C.; Wajid, M. A. *J. Polym. Sci.* **1953**, *12*, 109.
(5) Krigbaum, W. R.; Flory, P. J. *J. Am. Chem. Soc.* **1953**, *75*, 5254.
(6) McMillan, W. G.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276.
(7) See: Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971 (see also references therein).
(8) McKenzie, D. S. *Phys. Rep.* **1976**, *27C*, 35.
(9) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(10) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(11) Yethiraj, A.; Honnell, K. G.; Hall, C. K. *Macromolecules* **1992**, *25*, 3979.
(12) Dautenhahn, J.; Hall, C. K. *Macromolecules* **1994**, *27*, 5399.
(13) Bellemans, A.; Janssens, M. *Macromolecules* **1974**, *7*, 809.
(14) McKenzie, D. S.; Domb, C. *Proc. Phys. Soc.* **1967**, *92*, 632.
(15) Olaj, O. F.; Lantschbauer, W. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 985.
(16) Lal, M. *Mol. Phys.* **1969**, *17*, 57.
(17) Madras, N.; Sokal, A. D. *J. Stat. Phys.* **1988**, *50*, 109.
(18) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in FORTRAN*; Cambridge University Press: Cambridge, U.K., 1992.
(19) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

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