Registry No. H_2SO_4, 7664-93-9; HSO_3Cl, 7790-94-5; PEEK, 31694-16-3.

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Computer Simulation of Three-Dimensional Multiple-Chain Systems: Scaling Laws and Virial Coefficients

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ABSTRACT: The "scanning method" which has recently been developed for the Monte Carlo simulation of single polymer chains is applied to multiple-chain systems on a simple cubic lattice. By this method the partition function of the multiple-chain system can be estimated directly. Therefore a scaling law for the partition function which is equivalent to des Cloizeaux's famous scaling law for the osmotic pressure can be tested. Furthermore, the second and third virial coefficients can be extracted from the Monte Carlo data. The compatibility of the results with the scaling law for the osmotic pressure is discussed.

1. Introduction

In recent years the experimental and theoretical investigation of polymer solutions at moderate concentrations has made great progress.[1] A great deal of the theoretical investigations—especially Monte Carlo simulations—is based on the self-avoiding walk (SAW) model of polymer chains. In this lattice model the macromolecules are represented by chains of sites occupied by monomers and connected by links of the underlying lattice. All allowed multiple-chain configurations are equally probable, and the only interaction results from the condition that double occupancy of lattice sites is forbidden (excluded volume). One can assume solvent molecules to be attached to the lattice sites which are not occupied by monomers.

Despite the simplicity of the SAW model a lot of experimental results[2,3] for athermal solutions—these are solutions in good solvents for which only entropy effects are present—can be explained by this model very well. In particular, the SAW model includes the universal scaling laws[4-6] predicted by field-theoretic methods and confirmed by experimental results. The most important one is des Cloizeaux's scaling law for the osmotic pressure of polymer solutions which will be tested in the present paper by Monte Carlo simulation of multiple-chain systems on a five-choice simple cubic lattice.

In the next section the scaling law for the osmotic pressure will be transcribed into an equivalent scaling law for the partition function. This will be done because the partition function can be estimated directly by the "scanning method" which has recently been developed by Meirovitch[7,8] for the Monte Carlo simulation of single polymer chains. In the third section the scanning method applied in the present paper to the simulation of multiple-chain systems will be described in detail. The results of the Monte Carlo simulation will be presented in the fourth section. Besides the scaling function for the partition function the second and third virial coefficients will be estimated, and the unsettled question about the validity of des Cloizeaux's scaling law in three dimensions will be discussed. A brief summary concludes the paper.

2. Scaling Laws

The most important result gained by the application of field-theoretic methods to polymer solutions is the scaling

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law for the osmotic pressure.[5] For the SAW model on a simple cubic lattice with Q sites and lattice spacing a one has

$$a^3 \frac{\Pi}{kT} = \frac{N}{Q} F(x) \tag{1}$$

where Π is the osmotic pressure, N the number of polymers, T the temperature, k the Boltzmann constant, and F a universal function. For monodisperse polymer chains of n monomers (of $n - 1$ links on the lattice) each, one defines the concentration variable x by

$$x = (n-1)^{3\nu} \frac{N-1}{Q} \tag{2}$$

where $\nu = 0.59$ is the critical exponent for the end-to-end distance R of a single polymer chain ($\langle R^2 \rangle \sim (n-1)^{2\nu}$). In order to eliminate the influence of the chain length n and to obtain a scaling variable, the total volume of the system in eq 2 is measured in units of the single-chain volume, which is proportional to $(n-1)^{3\nu}$. The scaling law (1) is valid for large values of N, Q, and n as long as the monomer concentration is not too high. Introducing $N - 1$ instead of N in the definition (2) will simplify several subsequent equations (compare eq 6, 9, and 10).

From the scaling law (1) one can easily derive an equivalent scaling law for the partition function $Z(Q,n,N)$. Since no interaction energies are present in the SAW model (but only entropy effects) and since therefore all Boltzmann factors are equal to 1 the partition function $Z(Q,n,N)$ is just the number of possibilities to put N polymer chains of n monomers each on a lattice of Q sites without occupying any lattice site more than once. Using the definition of the osmotic pressure

$$a^3 \frac{\Pi}{kT} = \frac{\partial \ln Z(Q,n,N)}{\partial Q} \tag{3}$$

one arrives after integrating the scaling law (1) with respect to Q at

$$\frac{1}{N} \ln \frac{Z(Q,n,1)^N}{N!Z(Q,n,N)} = G(x) \tag{4}$$

$$F(x) = 1 + xG'(x) \tag{5}$$

and because of the definition (2) one has for $N = 1$:

$$G(0) = 0 \tag{6}$$

(the applicability of the scaling law (4) to small values of N will be discussed later; see eq 9).

The quantity $Z(Q,n,1)$ appearing in eq 4 (which is the number of configurations of a single chain on a lattice) is proportional to the number of lattice sites Q. More precisely

$$Z(Q,n,1) = \frac{Q}{2} A \mu^{n-1} (n-1)^{\gamma-1} \tag{7}$$

where A, μ, and γ are well-known constants.[9] By means of the scaling law (4) the unknown dependence of the partition function $Z(Q,n,N)$ on three variables is reduced to the unknown dependence of the universal function $G(x)$ on one variable.

In principle, a constant of integration depending on n and N should appear in eq 4. However, it will be shown now that in the limit $Q \rightarrow \infty$ the left-hand side of eq 4 (just as the right-hand side due to eq 6) goes to zero and therefore no constant of integration appears.

The partition function is expected to be a polynomial of degree N in Q (compare eq 7). More precisely one has

$$Z(Q,n,N) = \frac{1}{N!}\left\{ c_1(n)^N Q^N - \binom{N}{2} c_2(n) c_1(n)^{N-2} Q^{N-1} + \left[\binom{N}{3} c_3(n) c_1(n)^{N-3} + 3\binom{N}{4} c_2(n)^2 c_1(n)^{N-4} \right] Q^{N-2} + O(Q^{N-3}) \right\} \tag{8}$$

The first term describes the number of possibilities to put N polymers on the lattice without caring about double occupancies (from eq 7 one obtains $c_1(n) = {}^1/_2 A \mu^{n-1} (n-1)^{\gamma-1}$). By the second term all configurations with at least one intersecting pair among the N polymer chains are subtracted ($c_2(n)$ is identical with c_{nn} in the notation of Bellemans and Janssens[10] and with $-2c_{nn}$ in the notation of McKenzie and Domb[11]). Since in this way configurations with more than one intersection are subtracted several times the corresponding configurations with three intersecting polymers and two pairs of intersecting polymers have to be compensated by the third and fourth term, respectively. The expansion (8) is valid only if the boundary conditions can be neglected. For periodic boundary conditions this means that completely stretched configurations of two or three intersecting polymers have to be shorter than the sides of the underlying lattice because then for none of the terms considered in eq 8 additional forbidden configurations exist due to the boundary conditions. Using eq 8, one obtains

$$\frac{1}{N} \ln \frac{Z(Q,n,1)^N}{N!Z(Q,n,N)} = \frac{1}{2} \frac{c_2(n)}{c_1(n)^2} \frac{N-1}{Q} + \left(\frac{1}{2}\left(1 + \frac{1}{2(N-2)} \right) \frac{c_2(n)^2}{c_1(n)^4} - \frac{1}{6} \frac{c_3(n)}{c_1(n)^3} \right) \frac{(N-1)(N-2)}{Q^2} + O\left(\frac{1}{Q^3} \right) \tag{9}$$

In conclusion, it has been shown that the left-hand side of eq 4 goes to zero in the limit $Q \rightarrow \infty$ for arbitrary values of n and N and therefore no constant of integration appears in this equation. Furthermore, one reads off from eq 9 the first terms of the expansion of $G(x)$ with respect to x:

$$G(x) = G'(0)x + \frac{1}{2} G'(0)^2 \left(\rho + \frac{2-\rho}{N-1} \right) x^2 + O(x^3) \tag{10}$$

with

$$G'(0) = \frac{1}{2} \frac{c_2(n)}{c_1(n)^2} (n-1)^{-3\nu} \tag{11}$$

$$\rho = 4\left(1 - \frac{1}{3} \frac{c_3(n) c_1(n)}{c_2(n)^2} \right) \tag{12}$$

Equation 10 is not restricted to the limit $n, N \rightarrow \infty$ but moreover gives the deviation from the scaling function for arbitrary values of n and N. This fact will be important in the fourth section where the quantity ρ will be evaluated for small values of N. Due to the introduction of $N - 1$ in the definition (2) of x, $1/N$ corrections are absent in the linear term of eq 10.

Equation 5 which relates the function $G(x)$ to the scaling function for the osmotic pressure dictates the following n-dependence of the second virial coefficient (again the notation is taken from the paper of Bellemans and Janssens[10]):

$$A_2(n) = \frac{1}{2n^2} \frac{c_2(n)}{c_1(n)^2} = G'(0) \frac{(n-1)^{3\nu}}{n^2} \tag{13}$$

Furthermore, one sees from eq 5 and 10 that definition (12) coincides with the definition by des Cloizeaux and Noda[12] for the quantity ρ which is commonly used to characterize the third virial coefficient.

3. Monte Carlo Procedure

There exist a large number of papers on the Monte Carlo simulation of athermal polymer solutions.[13-26] In all these simulations—for the SAW model on two-dimensional[13-18] and three-dimensional lattices[15,19-24] as well as for a continuum model[25,26]—in each Monte Carlo step a multiple-chain configuration is changed locally in order to obtain a new configuration. In contrast, in the present paper a completely new configuration will be constructed in each Monte Carlo step as usual in the computer simulation of single chains (see for instance the review article by McKenzie[27] and references therein). In order to manage the problem of "sample attrition"—this is the loss of configurations by double occupancies—Meirovitch's "scanning method"[7,8] which is based on an old paper by Rosenbluth and Rosenbluth[28] was used for the simulation (recently, the original Rosenbluth algorithm has been used by Khalatur et al.[29] to simulate continuum systems of several chains).

With the scanning method a configuration is constructed by adding monomers with a step-by-step procedure, based on scanning in each step for allowed configurations (without double occupancies) in future steps. The probability for selecting a certain lattice site for the next monomer is proportional to the number of continuations starting with this lattice site. More precisely, the following procedure[7] was used for constructing configurations of N polymer chains of n monomers each on a five-choice simple cubic lattice of Q sites (cubes with periodic boundary conditions were used).

A starting point for the first polymer is selected out of the Q lattice sites with equal probability $1/Q$ and occupied by a monomer. Once the first k monomers have been placed at sites $s_1 ... s_k$ one counts for each of the six nearest neighbors s of site s_k the allowed continuations consisting of b further steps (for the monomers $k + 1 ... k + b$) and starting at site s. The probability for selecting one of the six nearest neighbors s of s_k for the $(k + 1)$th monomer is chosen proportional to the number of allowed continuations starting at site s (in this way the probability for selecting s_{k-1} for the $(k + 1)$th monomer vanishes of course). Then the $(k + 1)$th monomer is placed on the selected site s_{k+1}. In this way one has to place n monomers for the first polymer. If there is in any step no continuation possible, one selects a new starting point and repeats the procedure from the beginning.

Once the first polymer is placed on the lattice a starting point for the second polymer is selected out of the remaining $Q - n$ sites with equal probability, and the further $n - 1$ monomers of the second polymer are placed on the lattice according to the scanning method described above. A new starting point is selected again and again until the desired number of polymers is reached. If there is in any step of the procedure no continuation possible, one begins once more by selecting a new starting point for the first polymer.

Figure 1 shows for chains of length $n = 10$ on a lattice of $Q = 10^3$ sites the fraction of configurations without double occupancies. Crucial for the applicability of the scanning method to multiple chain systems is the observation that this function is not an exponentially decreasing function of the number of chains N but is nearly constant until it decreases rapidly at a certain critical value of N. Furthermore Figure 1 shows how this critical value can be raised by using a larger scanning parameter b, thereby improving the scanning method. However, for practical purposes b has to be small because computer time increases exponentially with b.

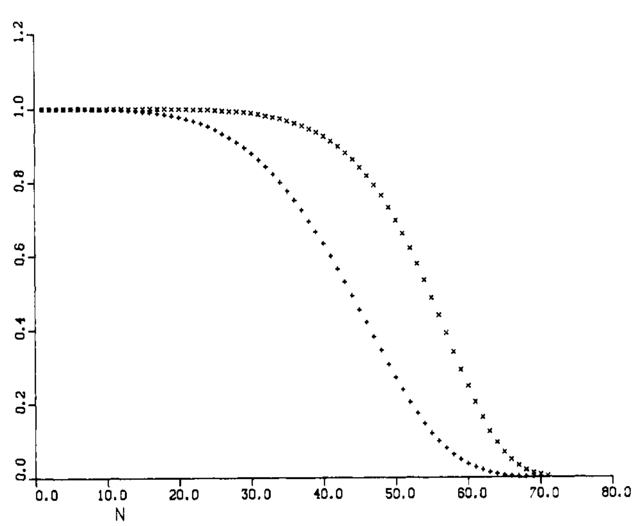

Figure 1. Fraction of configurations without double occupancies vs. number of polymer chains for two different scanning parameters (+, $b = 1$; x, $b = 2$). Chain length $n = 10$; number of lattice sites $Q = 10^3$.

So far only the construction of a configuration has been described. Now it will be explained how the partition function can be estimated. Since one knows in each step of the construction of a configuration the probability for selecting a lattice site for the next monomer, one can multiply all these single-step probabilities in order to obtain the probability $P_{i(t)}$ for constructing precisely the multiple-chain configuration $i(t)$ ($t = 1...T$, where T is the number of successfully completed among T_0 attempted multiple-chain configurations). Then, the quantity

$$\bar{Z}(Q,n,N) = \frac{1}{T_0}\sum_{t=1}^{T}\frac{1}{P_{i(t)}} \tag{14}$$

is an approximate expression for the partition function $Z(Q,n,N)$ of the SAW model because in the Monte Carlo simulation each configuration i is generated with probability P_i and therefore one has for large values of T

$$\bar{Z}(Q,n,N) = \frac{1}{T_0}\sum_{i}\frac{1}{P_i}T_0P_i = \sum_{i}1 = Z(Q,n,N) \tag{15}$$

where the sum is over all configurations i without double occupancies. Equation 14 makes possible a direct estimation of the partition function and therefore one can easily check the scaling law (4).

Calculating the inverse probability $1/P_{i(t)}$ for a certain configuration $i(t)$, one has to be very careful in order to avoid overflow errors since $P_{i(t)}$ is an extremely small number (for instance up to $N = 300$ polymer chains of length $n = 30$ will be put on a lattice of $Q = 30^3$ sites so that the probability for a special configuration is exceedingly small). This problem can be managed by multiplying the inverse probabilities after completion of each polymer during the construction of a multiple-chain configuration by a fixed factor (even then a range of several 100 orders of magnitude has to be available).

In the next section the results of a series of estimations of $Z(Q,n,N)$ based on eq 14 and 15 will be summarized and discussed.

4. Results and Discussion

First of all the scaling law (4) for the partition function $Z(Q,n,N)$ will be tested directly by the Monte Carlo pro-

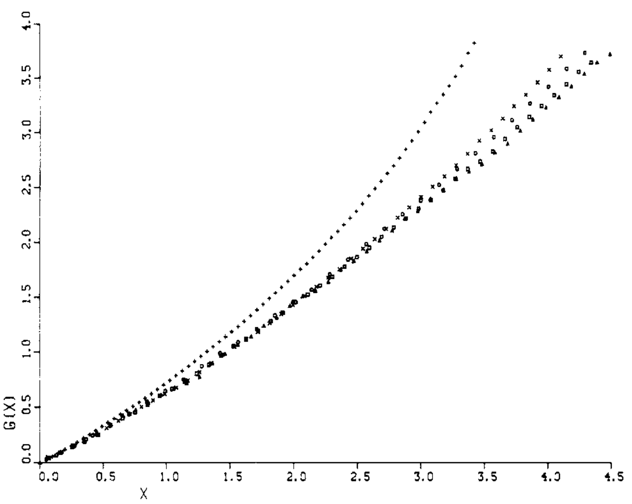

Figure 2. Scaling law for the partition function. +, $n = 10$, $Q = 10^3$; ×, $n = 20$, $Q = 20^3$; ○, $n = 30$, $Q = 30^3$; □, $n = 40$, $Q = 30^3$; △, $n = 60$, $Q = 30^3$.

cedure described in the preceding section. In order to calculate the scaling function $G(x)$ for multiple-chain systems, one has to know the number $Z(Q,n,1)$ of configurations of a single chain. The parameters fixing $Z(Q,n,1)$ according to eq 7 were taken from the paper by Watts[9] which is based on the extrapolation of exact results for short chains:

$$\mu = 4.6834 \qquad \gamma = 1.165 \qquad A = 1.17 \tag{16}$$

Figure 2 shows the results of simulations for different values of the chain length n and of the number of lattice sites Q. When the scanning parameter $b = 2$ (this is scanning for the possible continuations in the next two steps) was used, from 2000 to 5000 configurations were typically generated (a good hour of computer time on a Univac 1100/80 computer was used for each curve). The number of chains N goes from 1 to a maximum value which has been chosen so that the concentration x defined by eq 2 takes the values $0 \leq x \lesssim 4.5$. If one defines a critical concentration

$$x_c = \frac{(n-1)^{3\nu}}{\frac{4}{3}\pi\left(\frac{R}{a}\right)^3} \tag{17}$$

for which the volume of a sphere of radius R is available for each chain, one obtains, inserting for R the end-to-end distance (radius of gyration) of a single chain of n monomers, for x_c the approximate value 0.2 (3.6). Thus, for $x \lesssim 4.5$ the chains interpenetrate each other very strongly.

A first test for the Monte Carlo program is the fact that one obtains within the statistical error bars $G(0) = 0$. Therefore the properties of single chains are reproduced correctly. In order to estimate the statistical errors in all calculations, the total number of configurations has been divided into 10 groups for which the partition function has been calculated separately. The resulting error bars in Figure 2 are approximately of the size of the symbols. In Figure 2 for each chain length n the scaling function was plotted for only one value of the number of lattice sites Q ($Q = 10^3$ for $n = 10$, $Q = 20^3$ for $n = 20$, and $Q = 30^3$ for $n = 30$, 40, and 60) because curves for sufficiently large values of Q differ very little only. The function $G(x)$ for $N = 100$ ($Q = 30^3$) was omitted in Figure 2 because the error bars are five times larger than the size of the symbols and therefore the figure would otherwise become difficult to survey. However, within the error bars the results for $n = 100$ agree with the curves for $n = 40$ and $N = 60$ over the entire range of x.

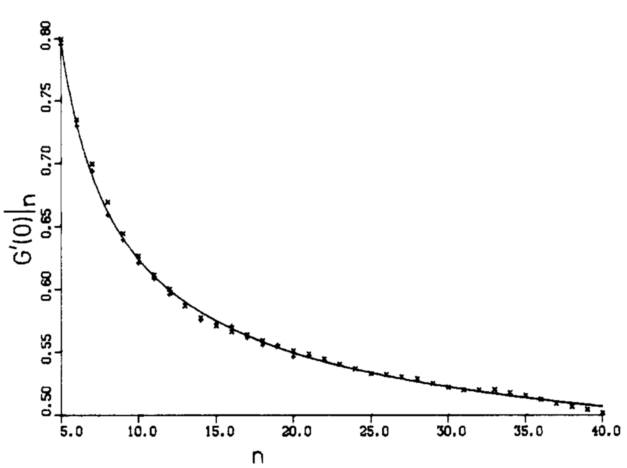

Figure 3. Dependence of $G'(0)|_n$ (eq 3) on the chain length n. Points: Monte Carlo data by Bellemans and Janssens.[10] Line: Scaling law with logarithmic corrections (eq 19).

Figure 2 seems to be in good agreement with the scaling law (4). For small values of n the estimated function $G(x)$ bends off from a universal scaling function, and the smaller the chain length n, the earlier the curve bends off. This behavior is due to the fact that the scaling law (4) becomes invalid for concentrated solutions. For

$$x_{\max} = (n-1)^{3\nu}\left(\frac{1}{n} - \frac{1}{Q}\right) \tag{18}$$

the lattice is completely filled with monomers, this is $x_{\max} = 4.8$ for $n = 10$, $Q = 10^3$, and the scaling law is of course invalid.

The nice confirmation of the scaling law for the partition function and thus of the equivalent scaling law for the osmotic pressure by Figure 2 implies a certain contradiction to the evaluation of the Monte Carlo data for the second virial coefficient by Bellemans and Janssens.[10] Taking for granted the scaling form $A_2(n) \sim n^{3\nu-2}$ (see eq 13) for the second virial coefficient, they found the result $\nu = 0.574 \pm 0.002$, which is slightly but significantly smaller than the commonly accepted value[12] $\nu = 0.588 \pm 0.001$. Another Monte Carlo test of des Cloizeaux's scaling law has been performed by Khalatur et al.,[29] who simulated off-lattice chains of length 40 at intermediate concentrations (corresponding to $0.5 \lesssim x \lesssim 6.5$ in the notation of the present paper) and studied the concentration dependence of the osmotic pressure. They found that des Cloizeaux's relation[5,12] $F(x) \sim x^{1/(3\nu-1)}$ is valid for these concentrations, however, with an even smaller value of $\nu(0.565 \pm 0.002)$. Recently, this discrepancy in the values of ν has been analyzed in more detail by computer simulation of multiple-chain systems.[30] Extrapolation of exact results for short chains in three dimensions leads to a violation of the scaling law[27] too (in two dimensions the scaling law for the osmotic pressure has been confirmed[18,27]).

In contrast to these deficiencies, the scaling behavior in Figure 2 is rather encouraging. Therefore, am empirical way to evaluate the Monte Carlo data for $A_2(n)$ in agreement with des Cloizeaux's scaling law shall be described briefly. If one calculates $G'(0)$ from the data by Bellemans and Janssens[10] using eq 13 with $\nu = 0.59$, one finds a slow variation of $G'(0)$ with chain length n (Figure 3); this is a violation of the scaling law for $n \lesssim 40$. At present the observed n-dependence of $A_2(n)$ cannot be accounted for by any theory.[31,32] Whereas mean field type calculations predict a logarithmic increase of $G'(0)$ with the chain length n[31] (the inadequate assumptions in these calculations have

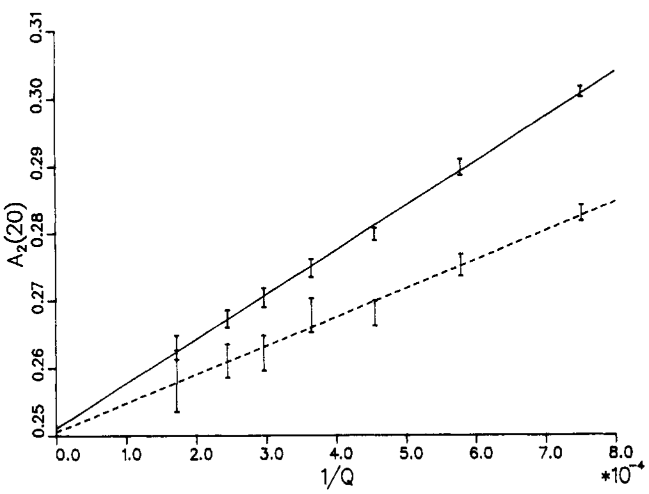

Figure 4. Second virial coefficient vs. inverse lattice size for chain length $n = 20$. Broken line: for $N = 5$ polymer chains. Continuous line: for $N = 10$ polymer chains.

been pointed out by Olaj and Lantschbauer[33]), Figure 3 indicates a logarithmic decrease of the form

$$G'(0)|_n = \frac{n^2}{(n-1)^{3\nu}} A_2(n) = a + \frac{b}{\ln (n-1)} \qquad (19)$$

The argument of the logarithm has been chosen to be $n - 1$ in order to improve the agreement with the Monte Carlo data. The results for a and b depend only slightly on the range of n used for the fit (19). Furthermore, if an arbitrary power of the logarithm is admitted in eq 19 and the data are analyzed by the least-squares method, the result for the power is very close to 1. These facts lead to the conjecture that eq 19 (or a similar equation) gives the correct dependence of $A_2(n)$ on n (see also Figure 3). The logarithmic corrections would lead to a (slightly) incorrect value of ν for small values of $n \lesssim 40$.

Using eq 19 one obtains from the data by Bellemans and Janssens $G'(0) = 0.33$ in the limit $n \rightarrow \infty$ (the same procedure with $\nu = 0.588$ instead of $\nu = 0.59$ gives a value that is some 10% larger). From the experimental and the renormalization group results given by des Cloizeaux and Noda,[12] one finds—taking into account the different definitions of the scaling variables x—$G'(0) = 0.31$ and $G'(0) = 0.35$, respectively (the conversion was performed with the value for the radius of gyration given by Bellemans and Janssens[10]). Therefore, the logarithmic corrections in eq 19 not only remove the discrepancy in the value of ν obtained from the Monte Carlo data in three dimensions but also lead to a quantitatively correct prediction for $G'(0)$ in the limit $n \rightarrow \infty$. However, since the logarithmic corrections in (19) are so far justified only empirically and since a common estimation of ν, a and b with eq 19 gives questionable results, eq 19 will not be used in the following.

Now the data for the partition function $Z(Q,n,N)$ obtained by the scanning method will be evaluated in more detail in order to estimate the second and third virial coefficients (more precisely: the quantities $A_2(n)$ and ρ defined by eq 12 and 13). To this end it is useful to define the approximation

$$A_2(n)|_{Q,N} = \frac{Q}{n^2} \frac{G(x)_{Q,n,N} - G(x)_{Q,n,N=1}}{N-1} \qquad (20)$$

for the second virial coefficient. Using eq 10, one obtains

$$A_2(n)|_{Q,N} = A_2(n) + n^2 A_2(n)^2 \left(1 + \frac{N-2}{2}\rho\right)\frac{1}{Q} + O\left(\frac{1}{Q^2}\right) \qquad (21)$$

Table I
Virial Coefficients Obtained by Monte Carlo Simulation of Multiple-Chain Systems

n	$A_2(n)$	ρ
7	0.3358 ± 0.0011	0.56 ± 0.02
10	0.3025 ± 0.0016	0.52 ± 0.02
20	0.2519 ± 0.0013	0.40 ± 0.02
30	0.2312 ± 0.0054	0.41 ± 0.09

Plotting $A_2(n)|_{Q,N}$ vs. $1/Q$ for fixed values of n and N, one obtains for sufficiently large values of Q a straight line from which $A_2(n)$ and ρ (for $N > 2$) can be read off. Figure 4 gives an example for $n = 20$ and two different values of N (for these calculations some 8 h of computer time on a Univac 1100/80 computer was used). After several test runs, the scanning parameter $b = 1$ has been chosen because the statistical error bars for the same amount of computer time were somewhat less than for $b = 2$. For $n = 7$, 10, and 30, similar (but less time-consuming) calculations have been performed. The results are summarized in Table I.

The results for $A_2(n)$ are in perfect agreement with earlier Monte Carlo simulations and the exact results for $n = 7$.[10] In view of the problems in extrapolating the data for $A_2(n)$ to large values of the chain length n the dependence of ρ on n is a completely open question. The values in Table I are consistent with the renormalization group value $\rho = 0.39$ given by des Cloizeaux and Noda[12] provided that for $n = 20$ the asymptotic value is nearly reached. A more precise estimation of ρ for longer chains would be very interesting.

5. Summary

des Cloizeaux's scaling law for the osmotic pressure of a polymer solution was tested for the SAW model on a five-choice simple cubic lattice by Monte Carlo simulation.

To this end the scaling law was transcribed into a scaling law for the partition function which can be estimated directly by the Monte Carlo procedure used in the present paper. The Monte Carlo procedure is based on the scanning method which was developed by Meirovitch for the simulation of single polymer chains and is well suited for the simulation of multiple chain systems, too.

The Monte Carlo results confirm des Cloizeaux's scaling law. Former methods for evaluating the Monte Carlo and exact enumeration data for the second virial coefficient which lead to slight but significant deviations from the scaling form might be misleading due to logarithmic corrections.

With a formula for extrapolating the second virial coefficient from finite lattices to the infinite lattice not only the second but also the third virial coefficient could be extracted from the Monte Carlo data presented in this paper.

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Surface Fluorination of Polymers in a Glow Discharge Plasma: Photochemistry

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ABSTRACT: The important role of the photon component of a glow discharge plasma is documented for the case of surface fluorination reactions of polymers. Photochemical reactions were carried out with a plasma glow discharge as a source of electromagnetic radiation only; polymer specimens were isolated from all other components of the plasma. Results establish that radiation in the vacuum-ultraviolet range is capable of enhancing the reactivity of polymer surface toward fluorine gas, consistent with what is known about the photochemistry and thermochemistry of the reactants.

Introduction

Glow discharge plasma reactions have been demonstrated to be effective in perfluorinating the surface regions of a variety of polymers.[1-3] A brief discussion of reaction kinetics has also been presented.[4] The mechanism of the gas–solid reaction is not completely understood, however, owing to the very complex nature of the plasma (gas) phase and its interaction with the polymer surface. To gain some insight into this type of reaction, we have investigated the photochemical interaction of plasma radiation with polymer films immersed in a fluorine-containing gas environment. The experiments aimed to establish whether or not photons from the plasma could enhance the fluorination reaction, and if so, to establish the nature of this process.

The electromagnetic radiation present in a glow discharge has sufficient energy to cause photochemical reactions in both the gas and solid phases. Dissociative absorption of radiation by diatomic fluorine gas is one of the many possible events in a plasma and is in this work the process of interest in the gas phase; photoexcitation and photoionization of saturated hydrogen- and fluorine-containing polymers are the important processes that may occur in the solid phase.

The absorption of radiation by fluorine gas has been investigated in the UV–visible (200–800 nm) region[5,6] and in the vacuum-UV (<200 nm) region.[7,8] The key conclusion is that fluorine will dissociatively absorb photons in the continuum between 210 and 450 nm, with a peak at 284.5 nm. However, the extinction coefficient is relatively low compared to other halogens.[9] It is not until below 100 nm that fluorine again absorbs dissociatively, this time to excited fluorine atoms. Examples of photoassisted halogenation reactions discussed in the literature include photochlorination of poly(vinyl chloride)[10] and photofluorination of organic molecules.[11] In these reactions, UV radiation is used to dissociate the halogen molecules, thereby initiating the chain reactions.

The photochemistry of polyethylene, the polymer most heavily studied in this investigation, is another important consideration in our reaction system. Because polyethylene does not contain any chromophores, a relatively large amount of energy is needed for electronic excitation. Partridge[12] and George et al.[13] have investigated the absorption of polyethylene in the vacuum-UV region. Absorption about 185 nm ($\pi \rightarrow \pi^*$) is attributed to unsaturation that is present as an impurity. A region of nonionizing absorption ($\sigma \rightarrow \sigma^*$) occurs at 130 nm, with a transition region between 160 and 130 nm. Photoionization is believed to occur below 120 nm. As fluorine atoms are substituted for hydrogen atoms on the polyethylene chain, the region of photon absorbance shifts to higher energy (shorter wavelength). This is confirmed by valence band X-ray photoelectron spectroscopy, which has been used to study a series of model fluoro polymers.[14]

The product of the interaction of the polymer with the photons is either an excited or an ionized species. An ionized polymer molecule will be readily converted to an excited neutral molecule by charge neutralization with a free electron. The excess energy present will be larger than

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