nitudes are obtained if more detailed models (e.g., Hall–Helfand[19] or Jones–Stockmayer[20]) are used. There is no quantitative way to extrapolate this result from 93 to 25 °C for comparison with the dielectric result; qualitatively, it looks as though some segmental flexibility is definitely present at the higher temperature. Again, data for a wide range of molecular weights and temperatures are needed.

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Scaling Power Laws for Semidilute Polymer Solutions. A Monte Carlo Simulation in Three Dimensions

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Introduction

In recent years considerable progress has been made in the understanding of semidilute solutions of long, flexible polymers.[1] Much of this progress is based on the discovery of a relation between polymer solutions and magnetic systems by De Gennes[2] and Des Cloizeaux.[3] One of the most important consequences of this relation is Des Cloizeaux's scaling law for the osmotic pressure Π of athermal polymer solutions (these are solutions in good solvents for which only entropy effects are present). If the polymers are represented by self-avoiding walks (SAW model) on a five-choice simple cubic lattice with lattice spacing a, this scaling law reads

$$a^3\Pi/kT = CF(C/C^*) \qquad (1)$$

where the concentration $C = N/Q$ is the number of polymers N divided by the number of lattice sites Q, T is the temperature, k is the Boltzmann constant, and F is a universal function. For monodisperse polymer chains of n monomers (that is, each polymer consists of n sites or $n - 1$ links on the lattice) the critical concentration is defined by

$$C^* = B^{-3}(n-1)^{-3\nu} \qquad (2)$$

where $\nu = 0.588 \pm 0.001$[4] is the exponent for the end-to-end distance R of a single polymer chain ($\langle R^2\rangle = B^2(n-1)^{2\nu}$, $B \approx 1$). The scaling law (1) is valid for large values of N, Q, and n as long as the monomer concentration is not too high ($nC \ll 1$). In the semidilute region ($C^* \lesssim C \ll 1/n$) the scaling function $F(x)$ is given by a simple power law:[3]

$$F(x) \sim x^{1/(3\nu-1)} \qquad (3)$$

Des Cloizeaux's scaling law for the osmotic pressure can be transcribed into an equivalent scaling law for the partition function $Z(Q,n,N)$:[5]

$$\frac{1}{N}\ln\frac{Z(Q,n,1)^N}{N!Z(Q,n,N)} = G\left(\frac{C}{C^*}\right) \qquad (4)$$

where the scaling function G is defined by

$$G(x) = \int_0^x \frac{F(x')-1}{x'}\,\mathrm{d}x' \qquad (5)$$

The quantity $Z(Q,n,1)$ appearing in eq 4 (which is the well-known number of configurations of a single chain on a lattice) is given by

$$Z(Q,n,1) = \frac{Q}{2}A\mu^{n-1}(n-1)^{\gamma-1} \qquad (6)$$

with $A = 1.17$, $\mu = 4.6834$, and $\gamma = 1.165$.[6] In the semidilute region one obtains in leading order from eq 3 and 5

$$G(x) \sim x^{1/(3\nu-1)} \qquad (7)$$

By means of the scaling laws (1) and (4) the unknown dependence of the osmotic pressure and of the partition function on three variables (Q, n, N) is reduced to the unknown dependence of the scaling functions on one variable (C/C^*).

Experimental results for the osmotic pressures of polymer solutions seem to be in good agreement with the scaling law (1).[7] However, exact enumeration studies and Monte Carlo simulations in three dimensions disagree slightly but significantly with the scaling law for the osmotic pressure.[8-13]

In the present letter the scaling law (4), (7) will be tested by a direct Monte Carlo estimation of the partition function for chains of length $n = 60$ and $n = 80$ on a simple cubic lattice. In contrast to a previous paper[5] where the properties (virial coefficients) of dilute solutions ($C \ll C^*$) have been estimated, the present letter is concerned with eq 7 for semidilute solutions ($C^* \lesssim C \ll 1/n$). In the next section the Monte Carlo procedure will be described in detail. The results and a discussion will be presented in the third section. A brief summary concludes the paper.

Monte Carlo Procedure

Recently, Meirovitch developed the "scanning method" for the Monte Carlo estimation of the entropy of single polymer chains.[14-17] Using this method which is based on an old paper by Rosenbluth and Rosenbluth[18] one has to scan for allowed continuations in future steps before adding a new monomer. It has been shown in a preceding paper[5] that the scanning method is well suited for the

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Monte Carlo simulation of multiple-chain systems too. In contrast to the usual Monte Carlo techniques for multiple-chain systems (a list of references can be found in ref 5) where a new configuration is constructed by a local change of a previous one, with the scanning method a completely new configuration is generated in each step.

In the present letter the scanning method will be used in its simplest form (scanning for allowed continuations in the next step only). More precisely, a multiple-chain configuration is constructed in the following way: If a new polymer has to be generated, a starting point is selected from the empty sites with equal probability. Further monomers are added to an existing polymer by choosing one of the empty nearest neighbors of the last monomer with equal probability. If all neighbors of the last monomer are occupied, one begins once more by selecting a new starting point for the first polymer.

Since one knows in each step of the construction of a multiple-chain 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

$$\bar{Z}(Q,n,N) = \frac{1}{T_0} \sum_{t=1}^{T} \frac{1}{P_{i(t)}} \tag{8}$$

is an estimation for the partition function of the SAW model. Namely, because 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 polymers of n monomers each on a lattice of Q sites without occupying any lattice site more than once. Because in the Monte Carlo simulation each configuration i is generated with probability P_i, one has for large values of T_0

$$\bar{Z}(Q,n,N) = \frac{1}{T_0} \sum_i \frac{1}{P_i} T_0 P_i = \sum_i 1_i = Z(Q,n,N) \tag{9}$$

where the sum is over all configurations i without double occupancies. Though by the scanning method the configurations are generated in a biased way, the mean value of the random variable $\bar{Z}$ is equal to Z for any value of T_0. The statistical fluctuations in $\bar{Z}$ (which can be estimated from several independent simulations) are reduced to zero in the limit $T_0 \rightarrow \infty$.

Results and Discussion

Equation 8 makes possible a direct estimation of the partition function and therefore one can easily check the scaling law (4), (7). This will be done in the following.

If the validity of the scaling law for the partition function is to be tested, it is important to choose the chain length n, the number of polymers N, and the size of the lattice Q as large as possible. Chains of length $n = 60$ and $n = 80$ could be simulated with a reasonable amount of computer time. Statistical error bars for the partition function lead not only to error bars ϵ for the scaling function G but also to a shift of the mean value of G of order $^1/_2 N\epsilon^2$ (this relation can be derived from eq 4). Therefore, reasonable results for G require that the error bar ϵ has to be very small. Because the shift in G increases with N, simulations for reasonably large values of N are very time-consuming (this fact prohibits simulations for a series of different values of the chain length n). Furthermore, the value of Q is limited by the fact that with increasing Q one has to raise the value of N in order to cover the same range of concentrations. For $n = 60$ extensive calculations with $N = 30$ polymers on a five-choice simple cubic lattice with $Q = 18^3$ sites have been perfomed. Then, up to some 30% of the lattice sites are occupied by monomers ($nC \lesssim 0.3$, $x = C/C^* \lesssim 7$). The edges of the cubic lattice cell (with periodic boundary conditions imposed) are clearly longer than the end-to-end distance $R \approx 12$ for chains with $n = 60$, and therefore finite size effects are expected to be small. In order to estimate the statistical errors the total number of about 3×10^6 configurations has been divided into 10 blocks of configurations for which the partition function has been calculated separately.

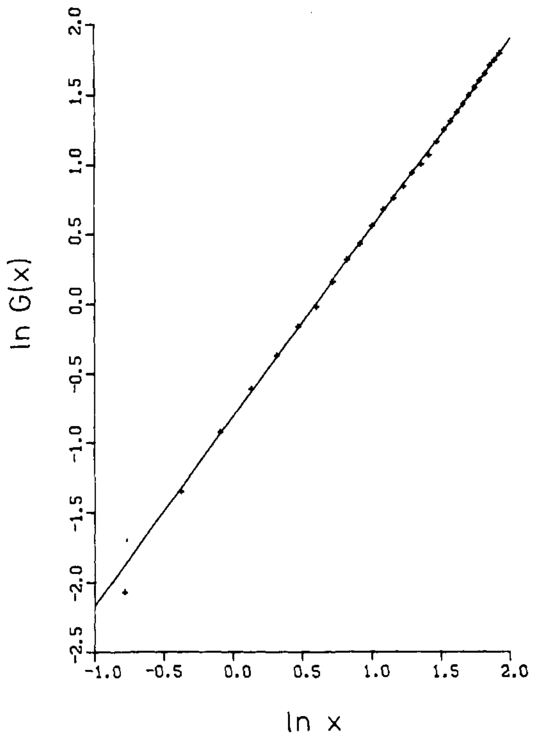

Figure 1. log-log plot of the scaling function $G(x)$ defined in eq 4 for chains of length $n = 60$.

Figure 1 shows the scaling function obtained for $n = 60$. The error bars are smaller than the size of the symbols. Even for surprisingly low values of $x = C/C^*$ ($x \gtrsim 0.7$) the data points lie on a straight line in the log-log plot, in perfect agreement with the scaling prediction (7). From the slope of the straight line one calculates the value of ν (one can see easily that the result for ν is independent of the value of ν used in the definition of C^*). The slope has been estimated by linear regression, where the lower bound for which the power law (7) was assumed to be valid was increased until no systematic variation of the result could be found. One obtains the value $\nu = 0.579 \pm 0.001$, which is only slightly smaller than the commonly accepted value $\nu = 0.588 \pm 0.001$.[4,7] This result is appreciably better than the value $\nu = 0.565 \pm 0.002$ obtained in a very similar way by Khalatur et al. by a Monte Carlo simulation of the osmotic pressure for continuum chains of length $n = 40$.

For chain length $n = 80$, 10^6 configurations consisting of $N = 30$ polymers on a lattice of $Q = 22^3$ sites have been generated. The resulting value of ν is 0.579 ± 0.002. Because the deviations from the commonly accepted value $\nu = 0.588 \pm 0.001$ are of the order $1/n$, the present results for $n = 60$ and $n = 80$ are in reasonable agreement with the scaling law for the partition function which is equivalent to Des Cloizeaux's scaling law for the osmotic pressure. The better agreement of the present value of ν

compared to previous studies[8-10] might be caused by the fact that these previous studies extracted ν at very small concentrations (from the second virial coefficient) whereas the present study is based on the semidilute region. However, for the finite chain length the scaling prediction might lead to approximations of different quality in different regions of concentration. Okamoto's value $\nu = 0.574$,[12] which has also been obtained in the semidilute region, is comparable to the present value.

Summary

The scanning method was used to estimate the scaling function for the partition function of the SAW model on a five-choice simple cubic lattice in the semidilute region.

The Monte Carlo results for the scaling function are in perfect agreement with the power-law behavior predicted by the polymer-magnet analogy. From the exponent, which is the same as for Des Cloizeaux's scaling function for the osmotic pressure, one obtains the exponent for the end-to-end distance $\nu = 0.579 \pm 0.001$ for chain length $n = 60$ and $\nu = 0.579 \pm 0.002$ for $n = 80$. These results are in reasonable agreement with scaling predictions because the deviations from the commonly accepted value $\nu = 0.588 \pm 0.001$ are of order $1/n$.

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Relaxation Times of a Random Copolymer

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The relaxation times of linear homopolymers[1,2] are well understood when the entanglement effects are not dominant. In this note, we present some results on the dependence of the relaxation times of a random copolymer on the randomly occurring bead friction coefficients. In infinitely dilute solutions where the hydrodynamic interaction among the beads is so strong that the relaxation times are independent of the bead friction coefficient, there should be no difference between the homopolymer and the random copolymer. On the other hand, at higher concentrations (but below the entanglement point) the hydrodynamic interaction is screened[3] and the differences in the bead friction coefficients are expected to significantly affect the chain relaxation times. The results presented below pertain to this Rouse regime.

The dynamics of a linear homopolymer with n beads and Kuhn step length l under Θ conditions is described by the Langevin equation[1,3]

$$\frac{\alpha \mathbf{R}_i}{\alpha t} + \frac{3k_{\mathrm{B}}T}{\zeta_{\mathrm{b}}l^2}\sum_{j=1}^{n}(2\delta_{ii} - \delta_{i,j+1} - \delta_{i,j-1})\mathbf{R}_j = \mathbf{f}_i \tag{1}$$

where $\mathbf{R}_i$ is the position vector of the *ith* bead, $\mathbf{R}_i/\alpha t$ is its time derivative, ζ_{b} is the bead friction coefficient, and $\mathbf{f}_i$ is the Brownian force acting on the *ith* bead arising from the thermal fluctuations in the solvent. In eq 1, $k_{\mathrm{B}}T$ is the Boltzmann constant times the temperature and the inertial effects have been ignored. The diagonalization of the Rouse matrix appearing in eq 1 gives the eigenvalues λ_ν of the matrix from which the relaxation times $\tau_\nu \equiv 1/\lambda_\nu$ are obtained. Depending on the nature of the time-dependent correlation function under consideration, a numerical factor of 2 may appear in the relation between τ_ν and λ_ν. We here call the inverse of λ_ν as the relaxation time τ_ν. For the case of random copolymers, we generalize eq 1 to

$$\frac{\alpha \mathbf{R}_i}{\alpha t} + \frac{1}{\zeta_i}\sum_{j=1}^{n}(2\delta_{ij} - \delta_{i,j+1} - \delta_{i,j-1})\mathbf{R}_j = \mathbf{f}_i \tag{2}$$

where ζ_i is a random variable. The random value of ζ_i clearly has two origins: random bead friction coefficient and the random Kuhn segment length. The calculation of the relaxation times thus involves the diagonalization of the random nonsymmetric marix of eq 2.

We have taken ζ_i to be a random variable taking a value of ζ_1 with the probability of $(1 - \sigma)$ and ζ_2 with the probability of σ. The data presented here correspond to the case of $\zeta_2/\zeta_1 = 10$, although the conclusions are independent of the numerical value of this ratio. The relaxation times for each sample obtained by the diagaonalization ofthe corresponding random matrix are then averaged over 100 samples. The average relaxation time of the longest mode is plotted vs. σ (which is the fraction of the second component) in Figure 1 for both the linear and ring chains. For the linear chain, the average relaxation time is linear in σ. For the uniform ring polymer, the Rouse modes are doubly degenerate. When the ring chain contains two components, the Rouse mode degeneracy is lifted and the two branches depend on σ nonlinearly. However, the average of these two branches depends on σ, similar to the case of linear chains.

For any value of σ, we have found for the linear copolymer that the average relaxation times ($\langle\tau_\nu\rangle$) of the lower modes are proportional to $\langle\zeta_i\rangle n^2$. The linear dependence of $\langle\tau_\nu\rangle$ on $\langle\zeta_i\rangle$ is demonstrated in Figure 2, where $\langle\tau_\nu\rangle/\langle\zeta_i\rangle$ is plotted vs. σ for the modes ν from 1 to 6. The corresponding plot for the ring random copolymer is presented in Figure 3. In this case the individual relaxation times of the two branches (belonging to a given original degeneracy) exhibit a nontrivial dependence on σ, while the average of these two relaxation branches is proportional to $\langle\zeta_i\rangle n^2$. The nonlinear dependence of the relaxation branches of cyclic copolymers on σ indicates that the random introduction of a second component in the polymer chain sequence affects the longest relaxation time more in the case of rings than the linear chains and that there exists an optimum concentration of the second component at which this effect is maximal. Also it is to

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