bounded from above by 1.8437...). It should be pointed out that for a single SAW the scanning method is comparable in efficiency to the enrichment method[4] and still significantly less efficient than the dimerization method[25,27] where chains of up to 10^4 steps have been studied. However, the advantage of the scanning method over these two methods is in its much better suitability to handle a large variety of other chain models, multiple-chain systems (see ref 3 and references cited therein), chains which are subject to boundary constraints such as boxes, surfaces, etc. (see ref 38–40 and references cited therein) and self-interacting SAWs.[17–19,41] The scanning method is also expected to be the most efficient simulation method for estimating the entropy.[42,43]

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Computer Simulation Technique for Calculating the Entropy of Polymer Chains, Based on the Scanning Method with a Mean-Field Parameter

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ABSTRACT: Recently I have suggested a technique, based on the scanning method, which enables one to extract the entropy of a polymer chain from a sample of chain conformations. This technique is further improved here, by incorporating a mean-field parameter, *m*, and applied as a test to self-avoiding walks (SAWs) on a square lattice. We study SAWs (longer than in previous work) which are unbounded in space and also SAWs which are bounded by relatively small "boxes". The results for the entropy of the unbounded SAWs improve significantly, as compared to those of previous work, without a significant increase in computer time. The results for the bounded SAWs, however, are only slightly improved. We show that the parameter should optimally be defined to fit the particular properties of a model.

Introduction

The concepts of the scanning method,[1–3] described in the preceding article[4] (ref 4 will be denoted as paper I), constitute the basis for a technique[5,6] which enables one to extract the entropy of chains from a relatively small sample of chain conformations. This technique has been applied preliminarily to self-avoiding walks (SAWs) on square and simple cubic lattices and to SAWs which are bounded by relatively small "boxes" of size $(2L + 1)^d$, where d is the dimensionality.[5] Recently the technique has been significantly improved for the special case of chain models with hard core potential.[6] In the present paper it will be extended to chains which also have finite attractive or repulsive interactions and it will be further improved by introducing a "mean-field" parameter in the same way as has been defined in paper I for the scanning method. The technique will again be applied to bounded and unbounded SAWs on a three-choice square lattice, which constitute a convenient test case, since the entropy is known, with high accuracy, from series expansion[1,8] and other studies (see below). The SAWs will be generated with the direct Monte Carlo (MC) method,[9] which has the following advantages: (1) It is *exact*, i.e., generates SAW i of N steps, with its ensemble probability P_i

$$P_i = C_N^{-1} \tag{1}$$

where C_N is the total number of SAWs. (2) The method, in contrast to other simulation methods,[10-12] enables one to calculate the entropy S

$$S = -k_B \sum_{\text{SAWs}} P_i \log P_i = k_B \log C_N \qquad (2)$$

where k_B is the Boltzmann constant. S is obtained from the ratio W_N/W_0 (see ref 5 and 6), where W_0 and W_N are the number of SAWs (of N steps) attempted and generated, respectively. This property is especially useful for the bounded chains for which series expansion estimates for S are not available. However, the direct MC procedure is extremely inefficient for generating long SAWs, due to "sample attrition", which limits our chain length to $N \leq 79$; this is, however, a significantly longer chain length than has been studied by us before.[5,6] As in our previous work[5,6] we are interested in S_{EV}, the contribution to the entropy due to the excluded-volume (EV) effect. With the direct MC method S_{EV} is (see ref 5 and 6)

$$S_{\text{EV}} = S_I - S \cong -k_B \log (W_N/W_0) \qquad (3)$$

where S_I is the entropy of ideal walks (eq I6, i.e., eq 6 of paper I).

Finally, it should be pointed out that our technique for the entropy is general in the sense that it can be applied to *any* macromolecular state. This is in contrast to other methods for estimating the entropy,[13-17] which are limited to the extreme cases of very small conformational fluctuations (e.g., harmonic fluctuations around the native structure of a protein[15-17]), or very large fluctuations at the Θ point, where the EV effect can be neglected.[13]

In the next section the theory of our technique will be developed and we shall rely in our explanation on the Theory section (B and C) of paper I.

Theory

Consider a sample of SAWs, generated with the direct MC method (or with any other *exact* simulation method); i.e., SAW i has been selected with the exact probability $P_i = C_N^{-1}$. Since a *large* sample in equilibrium can be obtained, in principle, by any exact simulation method, one can *assume* that the given sample has been constructed with the scanning method (employing certain values for the scanning parameter b and the mean-field parameter m—see paper I), rather than with the direct MC procedure. Thus, one can reconstruct for each step of SAW i the transition probability $p_k(\nu_k,b,m)$ (eq I22), with which the direction ν_k has *hypothetically* been chosen and define $P_i(b,m)$ (eq I23), the *unnormalized* probability of SAW i

$$P_i(b,m) = \tfrac{1}{4} \prod_{k=2}^{N} p_k(\nu_k,b,m) \qquad (4)$$

This probability leads to $P_i'(b,m)$

$$P_i'(b,m) = P_i(b,m) / \sum_{\text{SAWs}} P_i(b,m) = P_i(b,m)/A \qquad (5)$$

which is *normalized* over the ensemble of all SAWs.

It should be pointed out that, in contrast to the scanning method, the value of the normalization factor A is not obtained by the present procedure. Therefore, the entropy cannot be estimated either by $\langle S \rangle_{b,m}$ (eq I24) or by eq I32, which is based on "importance sampling", but rather by $S^{\text{A}}(b,m)$ where

$$S^{\text{A}}(b,m) = -k_B \sum_{\text{SAWs}} P_i \log P_i(b,m) \qquad (6)$$

One can also estimate S by $S^{\text{B}}(b,m)$ and therefore by $S^{\text{M}}(b,m)$ where

$$S^{\text{B}}(b,m) = -k_B \sum_{\text{SAWs}} P_i'(b,m) \log P_i(b,m) \qquad (7)$$

$$S^{\text{M}}(b,m) = [S^{\text{A}}(b,m) + S^{\text{B}}(b,m)]/2 \qquad (8)$$

In ref 6 we have argued that *for* $m = 1$ (i.e., the case where the mean-field parameter is not effective)

$$S^{\text{A}}(b,m) \geq S \qquad (9)$$

$$S^{\text{A}}(b,m) \geq S^{\text{B}}(b,m) \qquad (10)$$

Indeed, the results for $S^{\text{A}}(b,1)$ have always been found to overestimate the correct entropy S, in contrast to those of $S^{\text{B}}(b,1)$, which not only have satisfied eq 10 but, in most cases, have also underestimated S. These two opposing effects are canceled out to a large extent in S^{M}, which has led, therefore, to significantly more accurate results than both S^{A} and S^{B}.[6] We shall now prove that these relations (eq 9 and 10) also hold for $m \neq 1$. The proof is based on the relation

$$S = -k_B \sum_{\text{SAWs}} P_i \log P_i \leq -k_B \sum P_i \log P_i'(b,m) \qquad (11)$$

which is shown in ref 18 to be satisfied for *any* distribution $P_i'(b,m)$. Since $A \leq 1$ (see eq 5), always $P_i(b,m) \leq P_i'(b,m)$, which leads together with eq 11 to eq 9. (The proof of eq 10 is straightforward; for details see discussion for eq 11–16 in ref 6.) It is obvious that for practical values of b (and $b \ll N$) $P_i'(b,m) \neq P_i$, and hence, $S^{\text{A}}(b,m)$ overestimates S (eq 9). However, the best estimate for S can be obtained by minimizing $S^{\text{A}}(b,m)$ with respect to m at $m = m^*$. Alternatively, the optimal parameters m^* can be determined by minimizing $\Delta S(b,m)$, the fluctuation of S^{A}, with respect to m, where

$$\Delta S(b,m) = \{ \sum_{\text{SAWs}} P_i [S^{\text{A}}(b,m) + k_B \log P_i(b,m)]^2 \}^{1/2} \qquad (12)$$

$\Delta S(b,m)$ vanishes for $P_i(b,m) = P_i$ and is expected to decrease monotonically as the approximation improves.[19] It should be pointed out that for chain models with finite attractive or repulsive interactions the first criterion (i.e., minimizing $S^{\text{A}}(b,m)$) is still valid. However, for such models one should minimize the fluctuation of the free energy rather than that of the entropy.[21]

With the direct MC procedure a SAW is sampled with the exact probability $P_i = C_N^{-1}$ and therefore $S^{\text{A}}(b,m)$ can be estimated from a sample of n SAWs by $\bar{S}^{\text{A}}(b,m)$

$$\bar{S}^{\text{A}}(b,m) = -n^{-1} k_B \sum_{t=1}^{n} \log P_{i(t)}(b,m) \qquad (13)$$

where $i(t)$ is SAW i obtained at time t of the process. Similarly, $\Delta S(b,m)$ (eq 12) will be estimated by $\Delta \bar{S}(b,m)$. In order to estimate $S^{\text{B}}(b,m)$ (eq 7) one should first express it as a function of statistical averages with the sampling probability P_i (eq 8), i.e.

$$S^{\text{B}}(b,m) = -k_B \Big[\sum_{\text{SAWs}} P_i P_i^{-1} P_i(b,m) \log P_i(b,m) \Big] \Big/ \sum_{\text{SAWs}} P_i P_i^{-1} P_i(b,m) \qquad (14)$$

In ref 6 we have derived $\bar{S}^{\text{B}}(b,1)$, the estimator of $S^{\text{B}}(b,1)$, for the special case of chain models with hard core potential; in what follows $\bar{S}^{\text{B}}(b,m)$ will be derived for chains which also have finite attractive or repulsive interactions. In this case P_i, the ensemble probability, is

$$P_i = \exp(-E_i/k_B T)/Z \qquad (15)$$

where E_i is the energy of conformation i, T is the absolute

Table I
Results for the Entropy of Unbounded SAWs on a Three-Choice Square Lattice[a-d]

b	m^*	$S_{EV}{}^{A}(b,m^*)$	$S_{EV}{}^{A}(b,1)$	$S_{EV}{}^{M}(b,m^*)$	$S_{EV}{}^{M}(b,1)$	$\Delta S(b,m^*)$	$\Delta S(b,1)$
$N = 49$							
1	0.70	0.0770 (3)	0.0639 (1)	0.0981 (6)	0.097 (2)	0.0274	0.0291
4	0.88	0.10087 (6)	0.09926 (7)	0.1036 (2)	0.1035 (3)	0.0086	0.0101
7	0.93	0.10297 (4)	0.10262 (4)	0.10357 (7)	0.10357 (7)	0.0044	0.0054
DMC		0.1035 (2)	0.1035 (2)	0.1035 (2)	0.1035 (2)		
series		0.10365	0.10365	0.10365	0.10365		
$N = 59$							
1	0.71	0.0793 (4)	0.0646 (3)	0.1017 (7)	0.102 (4)	0.0252 (3)	0.0268
4	0.87	0.10349 (4)	0.10147 (6)	0.1063 (3)	0.1059 (1)	0.00818 (9)	0.0098
7	0.93	0.10588 (4)	0.10537 (3)	0.10667 (7)	0.10669 (7)	0.00454 (5)	0.0057
DMC		0.10675 (7)	0.10675 (7)	0.10675 (7)	0.10675 (7)		
series		0.10681	0.10681	0.10681	0.10681		
$N = 79$							
1	0.71	0.0816 (2)	0.0654 (2)	0.1050 (7)	0.107 (6)	0.02268 (6)	0.0236
4	0.87	0.10676 (4)	0.10416 (4)	0.1113 (4)	0.1114 (6)	0.00783 (5)	0.0094
7	0.92	0.10964 (3)	0.10883 (3)	0.11103 (8)	0.1110 (2)	0.00485 (4)	0.0059
DMC		0.11087 (3)	0.11087 (3)	0.11087 (3)	0.11087 (3)		
series		0.11106	0.11106	0.11106	0.11106		

[a] N is the number of steps in a walk, b is the scanning parameter, and m^* is the optimal mean-field parameter. [b] $S_{EV}{}^{A}(b,m)$ (eq 6 and 18) and $S_{EV}{}^{M}(b,m)$ (eq 8 and 19) are estimations for the entropy. $\Delta S(b,m)$ (eq 12) is the fluctuation of S^A. These results are expressed in Nk_B units where k_B is the Boltzmann constant. [c] DMC denotes results obtained with eq 3. "Series" denotes results obtained with a formula based on series expansion.[7,8] [d] The statistical error is denoted by parentheses. For example, 0.0770 (3) = 0.0770 ± 0.0003. The results for $\Delta S(b,m)$ are rounded off to three significant figures.

Table II
Results for the Entropy of SAWs on a Square Lattice, Bounded by a "Box" of Size $(2L + 1)^2$[a]

b	m^*	$S_{EV}{}^{A}(b,m^*)$	$S_{EV}{}^{A}(b,1)$	$S_{EV}{}^{M}(b,m^*)$	$S_{EV}{}^{M}(b,1)$	$\Delta S(b,m^*)$	$\Delta S(b,1)$
$N = 49, L = 12$							
1	0.85	0.0873 (1)	0.0843 (1)	0.127 (2)	0.125 (2)	0.0334	0.0345
4	1.02	0.12554 (8)	0.12549 (8)	0.1379 (6)	0.1380 (6)	0.0180	0.0181
7	1.08	0.1317 (2)	0.1312 (2)	0.1396 (4)	0.1400 (5)	0.0144	0.0151
DMC		0.1387 (2)	0.1387 (2)	0.1387 (2)	0.1387 (2)		
$N = 59, L = 14$							
1	0.84	0.0845 (2)	0.0807 (5)	0.1213 (9)	0.121 (2)	0.0297	0.0310
4	1.01	0.12167 (4)	0.12168 (5)	0.1344 (6)	0.1344 (6)	0.0161	0.0161
7	1.07	0.12784 (4)	0.12742 (7)	0.1362 (4)	0.1360 (4)	0.0126	0.0130
DMC		0.1347 (2)	0.1347 (2)	0.1347 (2)	0.1347 (2)		

[a] For details see explanations to Table I.

temperature, and Z is the partition function. Replacing P_i^{-1} in eq 14 by its explicit expression (eq 15) leads to

$$S^B(b,m) = -k_B\Big[\sum_{\text{SAWs}} P_i \exp(E_i/k_BT)P_i(b,m) \log P_i(b,m)\Big] \Big/ \sum_{\text{SAWs}} P_i \exp(E_i/k_BT)P_i(b,m) \quad (16)$$

and therefore $\bar{S}_B(b,m)$ is

$$\bar{S}^B(b,m) = -k_B\Big[\sum_{t=1}^{n} \exp(E_{i(t)}/k_BT)P_{i(t)}(b,m) \log P_{i(t)}(b,m)\Big] \Big/ \sum_{t=1}^{n} \exp(E_{i(t)}/k_BT)P_{i(t)}(b,m) \quad (17)$$

Obviously, in the case of hard-core interactions only, $E_i = 0$ for all i and the exponential terms in eq 17 drop out.

It should be pointed out that for an infinite sample $\bar{S}^B(b,m)$ will always lead to $S^B(b,m)$. However, for a finite sample size n the extent of convergence of $\bar{S}_B(b,m)$ depends on the standard deviations of the averages defining $S^B(b,m)$ (eq 16), which are functions of N, b, and m via $P_i(b,m)$. The closer $P_i(b,m)$ is to P_i, the smaller are the standard deviations and also the required sample size n. In this context it should be emphasized that the convergence of $\bar{S}^A$ to S^A is expected to be less sensitive to the accuracy of $P_i(b,m)$.

Since we are interested in the contribution to the entropy due to the EV effect, results will be presented for

$$S_{EV}{}^{A}(b,m) = S_I - S^A(b,m) \quad (18)$$

$$S_{EV}{}^{M}(b,m) = S_I - S^M(b,m) \quad (19)$$

See the derivation of eq 3.

Results and Discussion

Results for $S^A(b,m)$ (eq 6), $S^M(b,m)$ (eq 8), and ΔS (eq 12) for SAWs on a three-choice square lattice are presented in Tables I and II. The results in Table I are for chains, which are not restricted in space (unbounded); in Table II, however, we also study SAWs, which are bounded by relatively small "boxes" of size $(2L + 1)^2$ (i.e., the walls of the box are also excluded). Results are presented for three values of the scanning parameter, b = 1, 4, and 7, and for two values of the mean-field parameter m, the optimal value m^* and $m = 1$. SAWs of length N = 49, 59, and 79 have been generated with the direct MC procedure and the results are averages of results obtained for three samples, each of size $W_N \sim 6000$ ($W_N = n$), based on different random number sequences. As has already been pointed out in the Introduction, because of the strong sample attrition occurring with the direct MC method, we are limited to chain length of $N \leq 79$. In fact, the number of walks attempted (see eq 3) is $W_0 = 10^6$, 3.2×10^6, and 32×10^6 for N = 49, 59, and 79, respectively]; for the bounded SAWs $W_0 = 5.6 \times 10^6$ and 20×10^6 for N = 49 and 59, respectively. These values and the values for W_N, the number of SAWs generated, enabled us to estimate the entropy also from the asymptotically exact expression (eq 3). These results are denoted DMC in the tables. For the unbounded chains we also provide the series expansion estimates for the entropy obtained from the very accurate formula derived by Martin et al.[7] and Watts.[8]

In order to determine the optimal parameter m^* the program calculates for each value of b several ($\sim$10) estimates for S^{A}, S^{M}, and ΔS, based on different values of m. To save computer time, crude values of m^* have been initially determined from small samples of $\sim$500 SAWs. Approximately 2 h are required on the IBM 3081D computer to perform the entire calculation for N = 79 and $W_N \sim 6000$. It should be pointed out that the introduction of the mean-field parameter does not increase computer time significantly (see discussion in paper I).

Let us first discuss the results for the unbounded chains (Table I). As expected, the results for $S_{\mathrm{EV}}{}^{\mathrm{A}}(b,m)$ significantly improve as b increases and they always underestimate the DMC and the series expansion values, which are considered here to be exact. The results for $S_{\mathrm{EV}}{}^{\mathrm{A}}(b,m^*)$ obtained for the optimal parameter m^* are always better than those for $S_{\mathrm{EV}}{}^{\mathrm{A}}(b,1)$ obtained for $m = 1$ ($m = 1$ means that the optimal parameter is not effective). The effect of m^* turns out to be most pronounced for $b = 1$ and it decreases with improving the approximation, i.e., increasing the ratio b/N. Thus, for $b = 1$ the values of $S_{\mathrm{EV}}{}^{\mathrm{A}}$ obtained for m^* are 20–25% larger than thoss obtained for $m = 1$, upon going from $N = 49$ to $N = 79$, respectively; for $b = 4$ the corresponding values are 1.6–2.5% and for $b = 7$, 0.41–0.74%. Similar differences in the absolute value between the results for $\langle S_{\mathrm{EV}}\rangle_{6,m^*}$ and $\langle S_{\mathrm{EV}}\rangle_{6,1}$ have also been found in paper I. The best approximation for the entropy $S_{\mathrm{EV}}{}^{\mathrm{A}}(7,m^*)$ still leads to results which underestimate the correct values by $\sim$0.5%, 0.84%, and 1.3% for N = 49, 59, and 79, respectively. It should be noticed that similar deviations from the correct values have been also observed for the results for $\langle S_{\mathrm{EV}}\rangle_{6,m^*}$ in Table I of paper I and it is reasonable to expect that the values of $|S_{\mathrm{EV}}{}^{\mathrm{A}}(7,m^*) - S_{\mathrm{EV}}|$ and $|\langle S_{\mathrm{EV}}\rangle_{6,m^*} - S_{\mathrm{EV}}|$ will remain close also for longer chains; this means that for $N = 399$, for example, the result for $S_{\mathrm{EV}}{}^{\mathrm{A}}(7,m^*)$ should underestimate the correct value by $\sim$5% (see Table I of paper I). Such an approximation is certainly unsatisfactory and it can be improved only by increasing the scanning parameter b. It should be pointed out that the magnitude of the fluctuation $\Delta S(b,m)$ (eq 12) always decreases as the approximation improves; in particular the results satisfy $\Delta S(b,1) > \Delta S(b,m^*)$. It is also of interest to point out that the optimal values of m^*, obtained by minimizing $\Delta S(b,m)$, are always larger than but very close to, those obtained by minimizing $S_{\mathrm{EV}}{}^{\mathrm{A}}(b,m)$. For example, for $N = 59$ and $b = 4$ the values of m^* obtained by the two methods are respectively 0.91 and 0.87; for $b = 7$ they are 0.94 and 0.93.

We find (as in ref 6) that for all values of b the results for $S_{\mathrm{EV}}{}^{\mathrm{M}}(b,m)$ are always significantly better than the corresponding values obtained for $S_{\mathrm{EV}}{}^{\mathrm{A}}(b,m)$. The table reveals that for $b = 7$ (and in most cases also for $b = 4$) the results for $S_{\mathrm{EV}}{}^{\mathrm{M}}(b,m)$ are equal, within the statistical error, to the values obtained by series expansion and the direct MC method. However, the statistical error for $b = 7$ (less than 0.1%, for $m = m^*$) is always significantly smaller than that obtained for $b = 4$. The effect of the mean-field parameter is observed in the results for $b = 1$ (and for $N = 79$ also for $b = 4$ and 7), where the statistical error for $m = m^*$ is significantly lower than that for $m = 1$. It should be pointed out that the statistical error of $S_{\mathrm{EV}}{}^{\mathrm{M}}$ is larger than that of $S_{\mathrm{EV}}{}^{\mathrm{A}}$, which stems from the fact that $S_{\mathrm{EV}}{}^{\mathrm{B}}$ has a relatively large statistical error (see discussion for eq 17).

Confining the chain within the walls of a $(2L + 1) \times (2L + 1)$ box imposes additional long-range restrictions, which significantly increase the value of the entropy S_{EV}. The results for the entropy in Table II always improve as b is increased. However, the results for $S_{\mathrm{EV}}{}^{\mathrm{A}}$ are less accurate in Table II than in Table I. For $b = 7$, N = 49 and 59 these results underestimate the values obtained with the direct MC method by $\sim$5%. As in Table I the results for $S_{\mathrm{EV}}{}^{\mathrm{M}}$ are significantly better than those for $S_{\mathrm{EV}}{}^{\mathrm{A}}$ and they deviate from the DMC values by not more than 1%. It should be pointed out that the effect of the mean-field parameter on $S_{\mathrm{EV}}{}^{\mathrm{A}}$ is significantly smaller for the bounded chains than for the unbounded ones. This is reflected, for $b = 1$, for example, by the larger values for m^* in Table II ($m^* = 0.85$) than in Table I ($m^* = 0.70$). In order to understand these results one should bear in mind that for the unbounded chains the effect of $m < 1$ is to decrease the preference given by $P_i'(b,1)$ to the compact SAWs and to increase the probability of the open ones. The box, on the other hand, forces the chain to be more compact and therefore the value of m^* increases. In fact, for $b = 4$ and 7 we obtain $m^* > 1$. We have tried to improve the effect of the mean-field parameter for the bounded SAWs of $N = 59$, by defining a different parameter m_1 for the last 20 steps (since the end of the chain is expected to be affected by the walls of the box more strongly than its initial part). However, the results for $S_{\mathrm{EV}}{}^{\mathrm{A}}(b,m^*,m_1^*)$ did not improve significantly (since $m^* \cong m_1^*$). This means that a different definition of the parameter (or parameters) is required, which takes into account the effect of the box in a more efficient way.

To summarize, in our previous work[5,6] we have developed a technique, based on the scanning method, for calculating the entropy of macromolecules from a sample of conformations simulated with any method. In the present paper we incorporate into this technique a mean-field parameter, m, and test its effect for SAWs on a square lattice. We also extend the technique for the case of finite interactions. The conclusion is that for the unbounded SAWs one can gain significant improvement in accuracy without increasing significantly computer time. The effect of m becomes larger as the scanning parameter b decreases. For SAWs which are bounded by a box, m is found to be less effective. We conclude that m should be defined optimally to fit the particular properties of a model.

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(18) Since $P_i = C_N^{-1}$, eq 11 becomes $\log C_N^{-C_n} \geq \log \prod_{i=1}^{C_N} P_i'$. For $P_i' \neq P_j'$, always $P_i'P_j' < (P_i' + P_j')(P_i' + P_j')/4$. One can therefore replace P_i' and P_j' each by $(P_i' + P_j')/2$, which does not violate the normalization condition. Performing this change successively for different pairs i,j leads asymptotically to $P_i' = C_N^{-1}$, which proves the above inequality.
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Born–Green–Yvon Treatment of Concentrated Polymer Solutions

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ABSTRACT: The thermodynamics and configurational statistics of a concentrated polymer solution are treated by using the Born–Green–Yvon integral equation approach, and equations are derived for thermodynamic mixing quantities, including the noncombinatorial contribution to the entropy of mixing. These incorporate terms arising from bare potential interactions and correlations through third bodies. Using these results we investigate the shifts in the upper critical solution temperature as a function of the energy parameters.

I. Introduction

Developments in the theoretical treatment of concentrated polymer solutions have lagged behind those in the theory of small-molecule solutions. There are two major approaches in analyzing experimental data on polymer solutions. Flory–Huggins theory,[1] the polymer analogue of regular solution theory, is a lattice model in which expressions for the energy (ΔU_{mix}) and combinatorial entropy ($\Delta S_{\text{mix}} = \Delta S_c$) of mixing are formulated, assuming that the components are randomly mixed on the lattice. The free energy of mixing (ΔA_{mix}) is given by

$$\Delta A_{\text{mix}} = \beta^{-1}(s \log \phi_1 + N \log \phi_2 + \chi s \phi_2) \qquad (1)$$

where β is the inverse temperature in energy units, s is the number of solvent molecules, N is the number of polymer chains (each of which has n monomers), ϕ_1 and ϕ_2 are the volume (site) fractions of solvent and monomer, respectively, and χ, the interaction parameter, is defined by

$$\chi = \Omega\beta(\epsilon_{12} - {}^1\!/\!_2\epsilon_{11} - {}^1\!/\!_2\epsilon_{22}) \qquad (2)$$

Ω is the coordination number of the lattice and ϵ_{22}, ϵ_{12}, and ϵ_{11} are the monomer–monomer, monomer–solvent, and solvent–solvent interaction energies for the different kinds of nearest-neighbor interactions on the lattice.

Modifications to Flory–Huggins theory have involved more sophisticated estimates of ΔS_c[2] and, in particular, considering the ϵ's to be free, rather than potential, energies.[3] The latter tactic enables χ to be divided into an entropic (χ_S) and an enthalpic (χ_H) component; the former is taken to be a correction term representing the noncombinatorial contributions to ΔS_{mix}, while the latter is related to ΔH_{mix}. Often, however, χ_S is greater in magnitude than χ_H, and a molecular interpretation for χ_S has remained a problem.

Flory–Huggins theory is easy to apply and has been widely used in analyzing experimental data, yet it fails to explain one interesting property of polymer solutions: the second critical point (the lower critical solution temperature) which is reached upon raising the temperature of the mixture.

This phenomenon has been qualitatively understood by considering the large differences in thermal expansivities of the two components. Two theories, similar in appearance, have evolved, and both attempt to quantify this important feature. Corresponding states theory, developed by Prigogine et al.[4] and extended and widely applied by Patterson and co-workers,[5] was the first, but a later description of Flory[6] has been more widely used. In both treatments the pure and mixed components obey the same reduced equation of state, and the solution is assumed to be randomly mixed. The advantage of Flory's approach is that he relates the reduction parameters to experimentally determinable properties such as the density and thermal expansion and pressure coefficients of the pure components. One or two adjustable parameters are used, and the expressions for the various thermodynamic quantities contain terms which, separately, reflect the contact energy and free volume differences of the two components. A volume change on mixing is therefore incorporated and produces a negative (temperature-dependent) contribution to both ΔU_{mix} and ΔS_{mix}. The result is[7] that as the temperature is increased $-T\Delta S_{\text{mix}}$ becomes positive and eventually dominates, therefore yielding a positive ΔA_{mix} and hence a second critical point.

The equation-of-state theories have been successful in predicting trends and properties which the random-mixing description does not reflect; a drawback is that these treatments yield little insight on the molecular level as to the nature of the interactions which give rise to the bulk properties of the solution.

Detailed microscopic descriptions do exist for a single chain; a major advance in this area was the work of Edwards,[8] who considered the "growth" of a chain as a diffusion process in a field which, in turn, is generated by the presence of the other monomers. Recall that the mean square end-to-end length of a linear polymer has the asymptotic behavior

$$\langle R_n^2 \rangle \sim n^{2\nu} \qquad (3)$$

where $\nu = {}^3\!/\!_5$ for a single chain in a good solvent. The

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