

Monte Carlo Simulations of Free and Confined Walks in Reflecting Statistics

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Received October 17, 1996[®]

The entropy of confined walks in reflecting statistics has been estimated through Monte Carlo simulations and compared with the corresponding entropy in usual absorbing statistics. This comparison is primarily viewed as one involving two distinct problems in combinatorial analysis. However, the authors believe reflecting statistics may also find applications in physics, physical chemistry, or other fields. Arguments, e.g., are given in the Discussion, tending to show that for severely confined polymer chains usual absorbing statistics cannot apply, and therefore that reflecting statistics might be followed instead.

I. INTRODUCTION

The general problem of random walks encountering an absorbing or a reflecting barrier was first analyzed by Smoluchowski,¹ while studying aggregation phenomena, and subsequently further considered by Chandrasekhar.² Absorbing and reflecting barriers are defined as follows: if a random walk encounters an absorbing barrier, the walk is “absorbed” by the barrier and is being eliminated from the statistics; if on the other hand the walk encounters a reflecting barrier, it is “reflected” by the barrier, thus following another path and therefore is not being eliminated from the statistics. From the theoretical standpoint and in the case of random-flight walks (RFWs, there is no excluded volume, the walk can cross itself freely), concentration profiles near an absorbing barrier are obtained by solving the diffusion equation with the condition that c , the concentration, should be equal to zero at the barrier. The solution of the same equation with the condition $dc/dx = 0$ at the barrier, where x is a coordinate perpendicular to the barrier, corresponds to the reflecting barrier case.²

As far as absorbing and reflecting barriers are considered from the standpoint of polymer-chain statistics, the problem seems to emerge in the early 1950s in connection with adsorption phenomena and involves various authors.^{3–6} In particular, DiMarzio^{5a} and DiMarzio and McCrackin^{5b} pointed to the fact, already noticed by Silberberg,⁴ that in such adsorption phenomena the wall or barrier should be considered to be absorbing, and not reflecting, as assumed by earlier authors (i.e., in physical reality as well as in any proper chain-generation procedure, in order to count equally any possible configurations, when a walk hits the barrier, the walk should be eliminated from the statistics).

Now, in three dimensions, the barrier may be a plane, two parallel planes (two infinite directions allowed), a cylinder (one infinite direction allowed), or a closed surface (no infinite direction allowed). All these barriers may be considered either as absorbing or as reflecting. The resulting

properties (entropy, concentration profiles etc., ...) will depend on the nature of the barrier, leading either to absorbing or to reflecting statistics.

If we consider that the barrier is a closed surface the walks or chains are totally confined. The entropy of confined RFWs, considering that the confining boundary is absorbing, was solved analytically several decades ago.^{7,8} The same problem for self-avoiding walks (SAWs, the walk or chain has excluded volume so that it cannot cross itself) is much more difficult to deal with analytically. Scaling procedures may be used,⁹ but to the authors knowledge, there exists no exact analytical treatment, hence the interest in using Monte Carlo (MC) simulations to extract some basic features of such confined self-avoiding walks.

Confined walks and in particular confined SAWs are of interest in various fields of physical chemistry and more particularly so in polymer science: gel permeation chromatography, ultrafiltration, microemulsion polymerization, polymer chains in gels, and so on. Thus the properties of constrained or confined SAWs are of practical interest, and many papers have been devoted to the subject.^{10–33} However, as already noticed with respect to adsorption, these properties will depend on the statistics obeyed by the chains. The usual assumption is that AS always holds whatever the conditions. Nevertheless, arguments developed in the Discussion intended to show that this is not necessarily true in conditions of severe confinement. On the other hand, reflecting chain statistics may be of interest in the case of diffusion in spaces containing obstacles, in some aggregation phenomena and possibly in other fields of physics and of physical chemistry. The purpose of the present paper is however the MC estimate of the entropy of confined walks (whether SAWs or RFWs) in reflecting statistics (RS), viewed as a problem in combinatorial analysis of long chains. In other words, the problem is considered in its own right, without particular care for the moment for practical applications. It may be stated as follows: “A walker starting with equal probability anywhere on a two- or three-dimensional grid (which may be bounded or not bounded) performs a series of N -step walks, each step going from a given vertex

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[®] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

to an adjacent one on the grid. The walk grows up to completion under the condition that the walker never crosses a previous path of the uncompleted walk, and, if there is a boundary, he never crosses it. The walker is allowed to screen *one step* ahead for permitted directions (no crossing) and is bound to take with *equal probability* one of these permitted directions. If at some step there are no permitted directions to follow (the walker gets trapped in a nest), the uncompleted walk is discarded from the statistics and a new walk is initiated". The corresponding problem in absorbing statistics would have been stated as follows: "... he never crosses it. The walker is not allowed to screen ahead for permitted directions, he is bound to take with *equal probability* one of the a priori possible directions ahead, (the reverse direction being forbidden) without knowing if it leads or not to a crossing or transgression of the boundary (if any). If at any step he hits an already visited vertex on the grid, or if there is a boundary and he transgresses it, the walk is eliminated from the statistics and a new walk is initiated".

The question to be answered is "What the entropy of the above bounded or unbounded walks is, and how it can be estimated through MC simulations?"

As far as AS is considered, the problem has been addressed elsewhere.^{29,32} The purpose of the present paper is to address the same problem in RS, with the help of convenient parameters derived from the MC simulations. (To the authors knowledge, no other paper on confined chains obeying reflecting statistics is available.) In section II to follow are described in more detail the MC procedures we have used, and in section III the simulation results are given. Section IV is a discussion of the MC results and of possible applications of RS in polymer physical chemistry. The Conclusion, section V, is a general overview of the main points in the article.

II. MONTE CARLO PROCEDURES

For free (nonbounded) SAWs, there are two basic step-by-step procedures to generate static (as opposed to dynamic) Monte Carlo samples, i.e., the absorbing and the reflecting generation procedures defined at the end of the Introduction. Here the obstacles instead of being some barrier are the previously generated steps of the SAW. These procedures have been initiated respectively by Wall and his co-workers^{34,35} (also called in the literature simple sampling³⁶) and by Rosenbluth and Rosenbluth³⁷ (also called in the literature biased sampling³⁶ or kinetic growth walks³⁸). In what follows we shall consider chains with or without excluded volume (SAWs and RFWs, respectively). In the case of free RFWs, there is no point in distinguishing between the absorbing and reflecting procedures. If however a barrier or boundary is introduced, the difference appears also for RFWs, because close to the boundary the number of available directions ahead is reduced.

The relationships to follow will be derived in three dimensions; however, extension to other (in particular two) dimensions is immediate. For convenience, though this is not essential, all chains, whether SAWs or RFWs, will be considered to lie on the simple cubic lattice.

The main difference between the absorbing and reflecting generation procedures considered in the Introduction lies in the fact that while the absorbing generation procedure

weights equally all generated configurations, this is no more true in the reflecting generation procedure, where different configurations appear with different frequencies. If $v_j = w_j^{-1}$ is the frequency with which configuration j appears in the MC sample when using the reflecting procedure, one may recover usual absorbing statistics by weighting chain j by the factor w_j , where w_j is given by

$$w_j = \prod_{i=1}^6 (i)^{n(i,j)} / Z_{\max} \quad (1)$$

Here $n(i,j)$ is the number of instances in chain j of the sample; there were i available directions to continue generating the walk. Z_{\max} is given for an N -step walk by

$$Z_{\max} = 6 \times 5^{N-1} \quad (\text{SAWs}) \quad (2a)$$

$$Z_{\max} = 6^N \quad (\text{RFWs}) \quad (2b)$$

Since the *attrition* (i.e., the probability of failure of an initiated MC configuration) is always much larger in AS, one has often to use the weighted reflecting procedure (WRS) instead of AS, to obtain a convenient MC sample obeying usual AS. Here however we are essentially concerned with the nonweighted statistics of the Monte Carlo samples obtained through the Rosenbluth–Rosenbluth (RR) procedure, that is with Monte Carlo samples obeying reflecting statistics.

For a N -step RFW or SAW confined inside some boundary, it has been demonstrated elsewhere^{29b,c} that the number of configurations Z_N can be MC estimated using the following relationship:

$$Z_N = Z_{\max} W (1 - A_{RS}) K \quad (3)$$

Here W is defined through

$$W = \langle w_j \rangle = E^{-1} \sum_j w_j \quad (3')$$

where E is the sample size. A_{RS} in eq 3 is the attrition corresponding to the reflecting generation procedure (of interest only in the case of SAWs). This attrition originates in the fact that a chain being generated might become trapped in a nest. A_{RS} should not be confused with A_{AS} , the attrition originating in the violation of the no double occupancy condition of absorbing statistics (or, if there is a boundary, transgression of the boundary). As already indicated, A_{AS} and A_{RS} are not of the same order of magnitude, the latter being often negligible, unless the chain is large enough or confined in a space of dimensions comparable or smaller than those of the free chain. A_{AS} is always equal to zero for free RFWs (free AS-RFWs), but not for confined RFWs. A_{RS} , on the other hand, is always zero, whether the RFW (RS-RFW) is free or confined (a RFW, if it runs in a deadlock, due to the particular shape of the confining volume, it can always go backwards). Finally, K in eq 3 is the number of lattice sites confined inside the boundary. Both W and A_{RS} (the latter when not being identically equal to zero) are functions of the chain-length and the dimensions and shape of the confining boundary.

In AS, $S(N,V)$ being the entropy, function of the number N of steps in the chain and the dimensions and shape of the

confining boundary V , and k being the Boltzmann's constant, one has

$$S_{AS}(N, V)/k = \ln Z_N \quad (4)$$

where Z_N is given in eq 3. Using eq 4, the entropy and pressure of AS-SAWs and AS-RFWs confined inside cubes of varying diameter have been reported elsewhere.³² Here we wish to obtain the corresponding entropy $S_{RS}(N, V)$ for RS-SAWs and RS-RFWs. To this end, we notice that the frequency with which a given configuration j appears when the RR generation procedure is used is proportional to^{29,37,39}

$$v_j = (w_j)^{-1} = Z_{\max} / \prod_{i=1}^6 (i)^{n(i,j)} \quad (5)$$

so that the corresponding probability is

$$p_j = v_j / (\sum_m v_m) \quad (6)$$

where the index m runs over all possible configurations of the chain.

From Boltzmann's relationship for the entropy

$$S/k = -\sum_j p_j \ln p_j \quad (7)$$

it follows that

$$\begin{aligned} S_{RS}/k = & -\sum_j \{v_j / \sum_m v_m\} \ln \{v_j / \sum_m v_m\} = \\ & -[(Z(N, V)/Z(N, V))][\sum_j \{v_j / \sum_m v_m\} \ln v_j] + \\ & [(Z(N, V)/Z(N, V))][\sum_j \{v_j / \sum_m v_m\} \ln (\sum_m v_m)] \quad (8) \end{aligned}$$

From eq 8, after some simple algebra, one finds

$$S_{RS}(N, V)/k = S_{AS}(N, V)/k + \ln \langle v \rangle - [\langle v \ln v \rangle / \langle v \rangle] \quad (9)$$

where $\langle v \rangle$ is the mean value of the v_j parameter defined in eq 5 and $S_{AS}(N, V)$ is obtained from eqs 3 and 4. Equation 9 for the entropy has been derived on the assumption of a neutral with respect to the chains confining boundary (0, ∞ potential) and no nearest-neighbor chain-segment interactions other than those originating in the geometric exclusion property (in the case of SAWs). Thus, thermodynamics or adsorption phenomena are not taken into account in eq 9, as these topics lie beyond the scope of the present communication. However, eq 9 can be easily generalized to the case of thermodynamics and adsorption, simply by weighting properly each chain j in the sample through a proper Boltzmann factor correcting for the probability p_j given in eq 6.

Let us notice that in eq 5, Z_{\max} , according to whether we consider RFWs or SAWs, should be taken equal to 6^N or to $6 \times 5^{N-1}$. On the other hand, eq 9 is valid whether the chain is free or confined, a RFW, or a SAW. For a free N -step RFW, $\langle v \rangle = \langle w \rangle = W = 1$, so that $S_{AS}(N, \infty) = S_{RS}(N, \infty)$, and from eq 3, where $A_{RS} = 0$ (RFWs), $W = 1$, and $K = 1$ (no confinement), one obtains $Z_N = Z_{\max} = 6^N$, and $S_{AS} = S_{RS} = N \ln 6$, the expected result.

The software used was the same as in ref 32. SAWs or RFWs were step-by-step computer generated, either in free

space or inside cubes of varying edge length B , always embedded in the simple cubic lattice. A sample size E was specified (the standard value of E being 10^5 independent chain configurations) as well as the number N of steps in the chain and the edge length B of the cube, and then the run was begun. At the end of each run, were displayed on the computer screen the quantities $W = \langle w \rangle$, $\langle v \rangle = \langle w^{-1} \rangle$, $\langle v \ln v \rangle$, the variances of these parameters, the number Z_N of configurations obtained from eq 3, S_{AS}/k obtained from eq 4, and finally S_{RS}/k obtained from eq 9.

To trace the figures to follow it was found convenient to use reduced values B_o for the cube edge size B , defined through

$$B_o = (B - 1)/\langle r^2 \rangle^{1/2} \quad (10)$$

where $\langle r^2 \rangle^{1/2}$ was the root-mean-square end-to-end distance of the free (nonconfined) N -step chain.

To compare the entropy of a confined chain with that of the corresponding free chain (the latter been assumed to start from the same lattice site), one has to calculate the mean entropy per lattice site S^p of the confined chain. In AS, one clearly has

$$S_{AS}^p(N, V)/k = S_{AS}(N, V)/k - \ln K \quad (11)$$

where K is the number of confined lattice sites. By analogy, one can define in RS

$$S_{RS}^p(N, V)/k = S_{RS}(N, V)/k - \ln K \quad (11')$$

Of course, in AS as well as in RS, each specific confined lattice site has its own entropy of confinement, with a degeneracy due to symmetry considerations. In AS, if $Z_A(N, V)$ is the number of available configurations starting from a specific site A, the corresponding entropy will be $k \ln Z_A(N, V)$. In RS, the problem is compounded by the fact that the various configurations starting from A are not equally weighted, and therefore to calculate the entropy one has to revert to eq 7. However, at the level of sophistication of the present paper, the mean values over all confined lattice sites have been considered, thus smoothing out any differences between specific sites. Therefore, within this approximation, eq 11' is an appropriate definition of S_{RS}^p .

III. MONTE CARLO RESULTS

Table 1 displays the entropies S_{AS}^p/k and S_{RS}^p/k for free SAWs and RFWs, obtained respectively using eqs 4 and 9, from 10 to 448 steps. (The superscript p here means that we chose on the infinite lattice a specific vertex from which all chain configurations are started.) The same table also provides the difference $\Delta S^p/k = (S_{AS}^p - S_{RS}^p)/k$ between the absorbing and the reflecting entropy. Also displayed in this table is the quantity $C = 0.161 + 1.544N + 0.167 \ln N$. It is known that Z_N for SAWs is of the form^{9,40}

$$Z_N = C^{\text{te}} \mu^N N^{\gamma - 1} \quad (12)$$

where μ is the connectivity constant and γ an universal exponent. In three dimensions one has $\mu = 4.6835^{41}$ and $\gamma = 1.667^9$ and the constant is equal to 1.175.³² From these values the quantity C in column 2 has been calculated. The agreement between eq 12 and the MC expression, eq 3 for

Table 1. Monte Carlo Estimated Entropies S_{AS} and S_{RS} , in Absorbing and in Reflecting Statistics, Respectively, of Free (Nonconfined) Self-Avoiding Walks, as a Function of the Number N of Steps in the Walk^a

N	$C = S_{AS}^p/k$ (TH)	S_{AS}^p/k (MC)	S_{RS}^p/k (MC)	$\Delta S^p/k$
10	15.986	15.99	15.94	0.05
14	22.218	22.22	22.10	0.10
18	28.436	28.44	28.15	0.29
22	34.645	34.65	34.30	0.35
28	43.949	43.95	43.31	0.64
38	59.440	59.45	58.19	1.26
48	74.919	74.91	72.80	2.11
58	90.391	90.39	87.12	3.27
68	105.858	105.85	101.86	3.99
78	121.321	121.32	115.44	5.88
88	136.781	136.79	130.62	6.08
98	152.239	152.24	144.65	7.59
108	167.695	167.69	158.82	8.87
118	183.150	183.14	173.53	9.61
128	198.603	198.60	188.95	9.65
138	214.056	214.06	205.37	8.69
148	229.508	229.48	220.13	9.35
198	306.756	306.76	287.30	9.46
248	383.993	383.97	373.98	9.99
298	461.224	461.26	449.73	11.53
348	538.450	538.52	517.90	10.60
398	615.673	615.48	604.76	10.72
448	692.893	692.50	683.10	9.40

^a The difference between the two entropies is shown in column five. Column two also displays S_{AS} , now calculated from the relationship $Z_N = 1.175\mu^N N^{\gamma-1}$, where μ is the connectivity constant in the simple cubic lattice, and γ is a universal exponent. k is Boltzmann's constant. (See text.)

the number of configurations, and consequently the entropy is beyond expectations good. Only beyond 200 steps, small yet negligible deviations do appear. Thus, Table 1 provides a check of the consistency and relevance of both eqs 3 and 12.

Precision in the MC determination of S_{RS}^p is much less satisfactory. This is due to the fact that the variance of $\langle v \rangle = \langle w^{-1} \rangle$ is much more important than that of $\langle w \rangle$. For our MC samples of 10^5 independent chain configurations, the data for S_{RS}^p/k in the fourth column of Table 1 are good to within 1.0–1.5%. This means that the precision in the data of $\Delta S_{RS}^p/k$, in the fifth column of Table 1, is good to within 10–15% only. Qualitatively, this lack of precision of the S_{RS}^p data may be explained as follows: it certainly happens that in a MC sample of 10^5 or so configurations, a few chains will have an anomalously low w_j value (extended chains with relatively few nearest neighbors). The effect of these chains on the mean value $\langle w \rangle$ will be imperceptibly small, while upon inversion of these few w_j values to obtain $\langle w^{-1} \rangle$, very large values may be obtained, significantly contributing to the mean value of the latter quantity. However, it is almost certain from the values of $\Delta S^p/k = (S_{AS}^p - S_{RS}^p)/k$ given in Table 1 that this quantity tends to a limit as N increases, of the order of 10 e.u. This MC finding may be explained using the following mean-field argument (which however is not a rigorous demonstration): from eq 9 one has

$$[(S_{RS})_{N+1} - (S_{RS})_N]/k = [(S_{AS})_{N+1} - (S_{AS})_N]/k + \ln \langle v \rangle_{N+1} - \ln \langle v \rangle_N - [\langle v \ln v \rangle / \langle v \rangle]_{N+1} - \langle v \ln v \rangle / \langle v \rangle_N \quad (13)$$

Because of eq 12 one has $[(S_{AS})_{N+1} - (S_{AS})_N]/k = \ln \mu$, as

Table 2. Monte Carlo Estimated Entropies of N -Step Self-Avoiding Walks, Confined inside Cubes of Edge Length B as Indicated^a

$N = 18 \langle r^2 \rangle^{1/2} = 5.84$			$N = 38 \langle r^2 \rangle^{1/2} = 9.16$			$N = 58 \langle r^2 \rangle^{1/2} = 11.78$		
B	S_{AS}/k	S_{RS}^p/k	B	S_{AS}/k	S_{RS}^p/k	B	S_{AS}/k	S_{RS}^p/k
∞		28.15	∞		58.19	∞		87.12
23	37.12	24.97	35	69.37	50.42	45	101.07	80.28
18	36.16	24.89	28	68.49	51.44	36	100.19	80.65
12	34.30	24.63	21	67.22	51.62	27	98.93	80.35
11	33.83	24.52	17	66.14	51.63	23	98.12	79.27
10	33.27	24.42	14	64.96	50.88	18	96.67	79.64
9	32.59	24.26	11	63.03	51.12	15	95.29	79.22
8	31.70	23.98	10	62.07	50.59	12	93.05	78.77
7	30.50	23.45	9	60.80	50.04	9	88.32	76.15
6	28.73	22.48	8	59.04	48.96	8	85.30	73.61
5	25.69	20.46	7	56.40	47.47	7	80.57	69.90
4	18.47	14.73	6	51.96	44.14	6	71.59	62.20

$N = 78 \langle r^2 \rangle^{1/2} = 14.07$			$N = 98 \langle r^2 \rangle^{1/2} = 16.13$			$N = 128 \langle r^2 \rangle^{1/2} = 18.69$		
B	S_{AS}/k	S_{RS}^p/k	B	S_{AS}/k	S_{RS}^p/k	B	S_{AS}/k	S_{RS}^p/k
∞		115.44	∞		144.65	∞		188.95
30	130.03	109.32	30	160.68	141.25	39	208.04	187.26
23	128.57	109.62	24	159.28	140.20	30	206.58	186.27
19	127.27	108.30	18	156.91	138.62	24	204.90	184.71
16	125.70	107.75	15	154.65	137.61	21	203.80	183.43
13	123.24	106.36	12	150.78	133.30	17	201.20	182.91
11	120.34	106.03	10	145.53	130.44	13	195.84	176.60
9	115.15	100.41	9	141.26	126.49	11	190.03	173.75
8	110.60	96.81	8	134.58	120.23	9	179.80	163.47
7	102.79	90.79	7	121.77	109.57	8	168.39	152.99
6	86.53	76.62						

^a Columns two display the overall entropy S_{AS} of the confined chain in absorbing statistics, estimated using eqs 3 and 4 in the text. Column three display the entropy per confined lattice site S_{RS}^p in reflecting statistics. This is obtained from the overall entropy S_{RS} through the relationship $S_{RS}^p/k = S_{RS}/k - \ln K$, where K is the number of confined lattice sites. S_{RS} itself is Monte Carlo estimated using eq 9 in the text.

the contribution from the factor $(\gamma - 1)\ln N$ is negligible for large N . Now one may assume that for N being sufficiently large, adding one more steps to each possible N -step configuration will in the mean be possible in μ different ways, so that according to its definition, eq 5, one also has $\langle v \rangle_{N+1} = \mu \langle v \rangle_N$, so that $\ln \langle v \rangle_{N+1} - \ln \langle v \rangle_N = \ln \mu$. Finally, replacing also $\langle v \rangle_{N+1}$ by $\mu \langle v \rangle_N$ in the third term in the r.h.s. of eq 13, one easily finds a contribution equal to $-\ln \mu$. In total, $[(S_{RS})_{N+1} - (S_{RS})_N]/k$ varies by $\ln \mu$ for each step added, the same quantity as $[(S_{AS})_{N+1} - (S_{AS})_N]/k$, and therefore the difference $(S_{AS} - S_{RS})/k$ becomes constant as soon as the above mean-field argument applies. MC simulations show this difference to be about 10 e.u.

Table 2 displays S_{AS} , the overall entropy in absorbing statistics, calculated from eqs 3 and 4, and S_{RS}^p , the entropy per lattice site in reflecting statistics, calculated from eqs 4, 9, and 11', for SAWs of various step lengths, as a function of the cube edge length B . If desired, S_{AS}^p , the entropy per lattice site in absorbing statistics may be easily calculated through eq 11. For illustration, the values of $\langle v \rangle$ and $\langle v \ln v \rangle$, to be used in eq 9 to determine S_{RS} , are given in Table 3 for $N = 18, 38, 58$, and 98 steps. Table 4 displays the same quantities as Table 2 for RFWs, and Table 5 displays the corresponding parameters $\langle v \rangle$ and $\langle v \ln v \rangle$.

In Figure 1 are shown the entropy variations ΔS^p per lattice site from the free state of the chain, for chains of 18 steps, as a function of B_0 , the reduced edge length of the cube for AS-SAWs, RS-SAWs, AS-RFWs, and RS-RFWs. It is seen that in RS, the entropy variation per lattice site decreases

Table 3. Mean Parameters $\langle v \rangle$ and $\langle v \ln v \rangle$ (See Text), Permitting the Monte Carlo Estimate of S_{RS} , the Entropy of N -Step Confined Self-Avoiding Walks in Reflecting Statistics^a

$N = 18$			$N = 38$		
B	$\langle v \rangle$	$\langle v \ln v \rangle$	B	$\langle v \rangle$	$\langle v \ln v \rangle$
∞	2.85×10^0	3.60×10^0	∞	2.85×10^1	1.31×10^2
23	5.97×10^1	4.17×10^2	35	9.95×10^4	1.99×10^6
18	9.82×10^1	7.22×10^2	28	8.92×10^4	1.59×10^6
12	2.67×10^2	2.15×10^3	21	2.16×10^5	4.01×10^6
11	3.73×10^2	2.77×10^3	17	5.20×10^5	1.02×10^7
10	4.32×10^2	3.60×10^3	14	1.29×10^6	2.63×10^7
9	5.76×10^2	4.87×10^3	11	1.76×10^6	3.80×10^7
8	8.66×10^2	7.49×10^3	10	3.16×10^6	6.29×10^7
7	1.46×10^3	1.31×10^4	9	5.67×10^6	1.14×10^8
6	3.43×10^3	3.27×10^4	8	1.24×10^7	2.54×10^8
5	1.72×10^4	1.87×10^5	7	3.99×10^7	8.40×10^8
			6	4.48×10^8	1.03×10^{10}

$N = 58$			$N = 98$		
B	$\langle v \rangle$	$\langle v \ln v \rangle$	B	$\langle v \rangle$	$\langle v \ln v \rangle$
∞	5.95×10^2	5.69×10^3	∞	1.54×10^6	3.48×10^7
45	4.52×10^7	1.19×10^9	46	3.10×10^{14}	1.33×10^{16}
36	1.64×10^8	4.52×10^9	30	4.41×10^{14}	1.90×10^{16}
27	1.49×10^9	4.59×10^{10}	24	3.21×10^{15}	1.46×10^{17}
23	1.25×10^9	3.73×10^{10}	18	2.38×10^{16}	1.15×10^{18}
18	2.09×10^9	6.06×10^{10}	15	5.68×10^{16}	2.72×10^{18}
15	5.98×10^9	1.82×10^{11}	12	4.99×10^{19}	2.83×10^{19}
12	9.76×10^9	2.88×10^{11}	10	3.20×10^{18}	1.63×10^{20}
9	7.60×10^{10}	2.37×10^{12}	8	1.60×10^{21}	9.23×10^{22}
8	2.71×10^{11}	8.72×10^{12}	7	1.76×10^{24}	1.14×10^{26}
7	3.91×10^{12}	1.34×10^{14}			
6	5.46×10^{14}	2.10×10^{16}			

^a B is the edge length of the confining cube.

more slowly than in AS, as B_0 is increased to large values. On the other hand, when B_0 is decreased below one, all curves seem to aggregate to nearly (but not exactly) the same curve. The curves corresponding to AS lie however always below those corresponding to RS. Figure 2 displays $\Delta S^p/k$ in RS as a function of the reduced cube side size B_0 , for chain lengths varying from 18 to 128 steps. The pattern found for ΔS^p as a function of N is at first sight surprising: ΔS^p first increases with N , reaches a maximum in the vicinity of N equal 58 steps, and then decreases with increasing N . We shall come back to this rather unexpected phenomenon in the discussion. At low B_0 values, all curves seem to aggregate to a single curve. This is more clearly apparent in Figure 3, which shows the region below $B_0 = 1$ for $N = 58, 98$, and 128 steps.

Figure 4 displays $\Delta S^p/k$ versus B_0 for RS-RFWs for $N = 18, 38, 58$, and 98 steps. The inversion occurring in RS-SAWs is not here observed, and ΔS^p regularly increases with N , all curves having again a tendency to aggregate as B_0 is decreased to low values. In Figure 5 are displayed the AS and RS behaviors of the larger chains investigated, in the case of lower values of B_0 .

IV. DISCUSSION

The ΔS^p_{RS} Behavior of Self-Avoiding Walks. Regarding the MC results of section III, the first point deserving a discussion is the peculiar behavior for SAWs of ΔS^p_{RS} , the entropy change per lattice site due to confinement, completely at variance with the corresponding behavior of the same quantity for RFWs: ΔS^p_{RS} , for a fixed B_0 value, first increases with N , up to some value in the vicinity of 58 steps, and then decreases upon further increasing N . It is very improbable that this at first sight surprising result can be attributed to some undetected flaw in our software, which

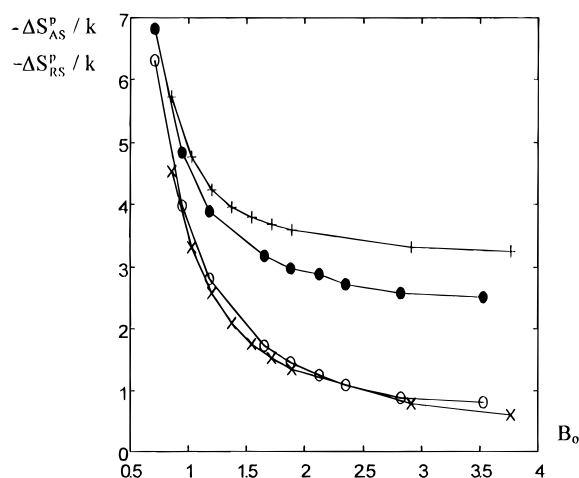
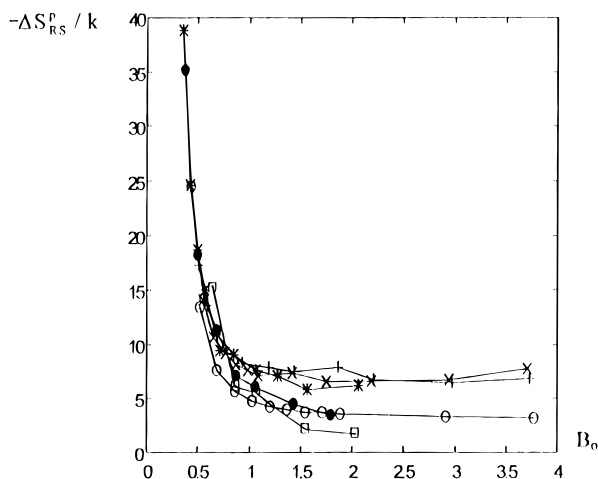
has been thoroughly tested. Further, the reproducibility of the MC values of S^p_{RS} is good, within the range of precision of 1.0–1.5% per run of 10^5 configurations, as above indicated. Therefore, we shall put forward the following argument, in order to explain this peculiar behavior: first, one may observe that for B_0 large enough, chains generated inside the cube will have a non-negligible probability of interacting with the confining boundary, only if the first step of the chain lies at a distance of less than $b\langle r^2_0 \rangle^{1/2}$, where $\langle r^2_0 \rangle^{1/2}$ is the root-mean-square end-to-end distance, and b is some constant lying between one and two (the exact value of b is to some extent arbitrary, and anyway is unimportant for the argument to follow). It is then easy to show that using the reduced variable B_0 , the fraction of chain configurations interacting with the boundary is constant, being independent of N . Now, considering only the interacting chains, when N is increased, more steps of the chains will in the mean interact with the boundary. Thus, the larger the N , the larger the proportion of interacting chains being generated that will have a chance of being trapped near the boundary, and thus being excluded from the statistics. But these excluded chains are those which in the mean would have displayed the largest v_j values (eq 5), had they been completed. Therefore, this “trapping effect” will reduce the overall mean value $\langle v \rangle$ of the MC sample. Going back to eq 9, we observe (see Tables 3 and 5), that when $\langle v \rangle$ decreases, the quantity of interest $\ln \langle v \rangle - \langle v \ln v \rangle / \langle v \rangle$ also decreases (in absolute value). Therefore S^p_{RS} will be larger than otherwise expected, and consequently the difference $\Delta S^p_{RS} = S^p_{RS}(N, \infty) - S^p_{RS}(N, B_0)$ will be smaller. Accordingly, the increase and then decrease of ΔS^p_{RS} for SAWs when N increases may be explained as follows: at first, for small N values, the trapping effect is small, and ΔS^p_{RS} increases with N as is the case for RFWs. Upon further increasing N , the trapping effect becomes increasingly important, first keeping ΔS^p_{RS} to a standstill and then overwhelming the “natural” increase of ΔS^p_{RS} , thus producing a decrease of this quantity. In support of this argument, Table 6 displays first the attrition of free SAWs ($B_0 = \infty$), then that when the chains are confined inside cubes of reduced edge length equal to two, and finally the difference between the two. To a good approximation, the difference $A_{RS}(B_0 = 2) - A_{RS}(\infty)$ is the excess attrition due to the effect of the boundary, and it is seen that this excess attrition regularly increases with N . Therefore, a larger proportion of chains which would have displayed large v_j values are excluded from the statistics when N is increased. Finally the fact that for RFWs, where no trapping can occur, ΔS^p_{RS} is a monotonously increasing function of N is also in support of the above argument.

Let us point out that the present discussion is irrelevant in the paragraph to follow (Possible Practical Applications of RS). Here we are concerned with relatively large values of B_0 , that is not severely confined chains, in which case it does not seem that RS might have applications in the field of polymers. However, the discussion is relevant with respect to the general combinatorial problem as stated in the Introduction, that is of the walker on an unbounded or bounded grid.

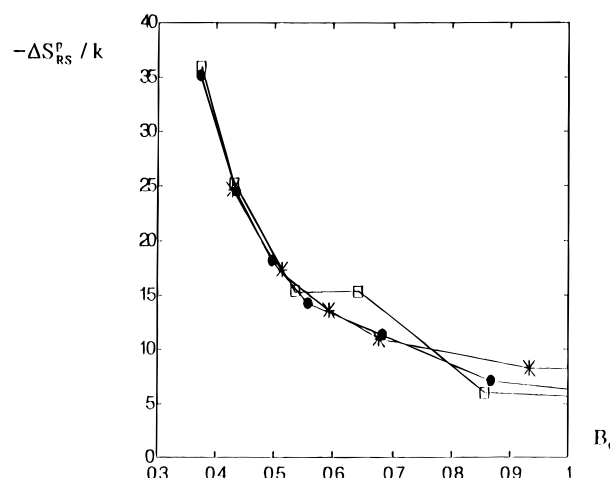
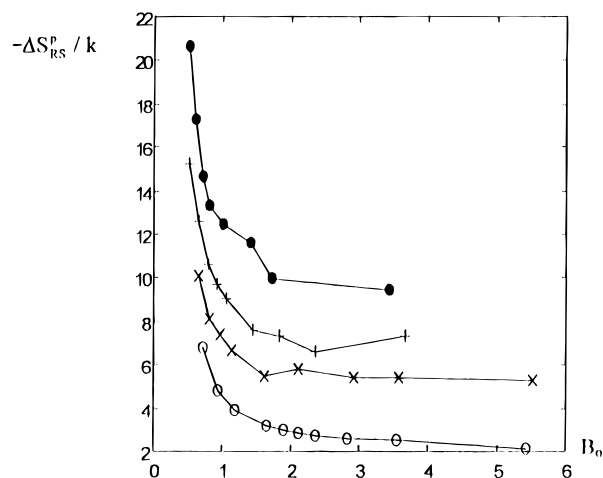
Possible Practical Applications of RS. Though as indicated in the Introduction the spirit of the present article is a study in its own right of the entropy of confined chains having reflecting statistics, it is nevertheless of interest to

Table 4. Same Entropies S_{AS} and S_{RS} as in Table 2, for Random-Flight Walks

$N = 18 \langle r^2 \rangle^{1/2} = 4.243$			$N = 38 \langle r^2 \rangle^{1/2} = 6.164$			$N = 58 \langle r^2 \rangle^{1/2} = 7.615$			$N = 98 \langle r^2 \rangle^{1/2} = 9.900$		
B	S_{AS}/k	S_{RS}^p/k	B	S_{AS}/k	S_{RS}^p/k	B	S_{AS}/k	S_{RS}^p/k	B	S_{AS}/k	S_{RS}^p/k
∞		32.25	∞		68.09	∞		103.92	∞		175.59
16	39.58	29.74	23	76.62	62.69	29	113.18	96.62	35	185.35	166.18
13	38.82	29.66	19	75.83	62.69	19	111.35	96.29	27	184.23	166.45
11	38.07	29.54	14	74.40	62.27	17	110.79	94.90	18	182.13	165.63
9	37.05	29.29	11	73.04	62.58	15	110.13	96.62	15	180.89	164.01
8	36.36	29.08	9	71.63	61.95	12	108.71	96.33	11	178.03	163.11
7	35.48	28.81	8	70.61	61.45	9	106.23	94.85	9	175.34	162.12
6	34.27	28.34	7	69.23	60.72	8	104.86	94.20	8	173.31	160.12
5	32.43	27.41	6	67.24	60.00	7	102.97	93.30	7	170.46	158.32
4	29.23	25.43	5	64.04	58.00	6	100.26	91.30	6	166.03	154.99
						5	95.59	88.87			

**Figure 1.** Entropy change $-\Delta S^p$ per lattice site due to confinement in absorbing and in reflecting statistics, for an 18-step chain, as a function of the reduced edge length B_0 of the confining cube: \circ , random-flight walks in absorbing statistics; \bullet , random-flight walks in reflecting statistics; \times , self-avoiding walks in absorbing statistics; $+$, self-avoiding walks in reflecting statistics.**Figure 2.** Entropy change $-\Delta S^p_{RS}$ per lattice site due to confinement, for self-avoiding walks in reflecting statistics, for various chain lengths, as a function of the reduced edge length B_0 of the confining cube: \circ , 18 steps; \times , 38 steps; $+$, 58 steps; $*$, 78 steps; \bullet , 98 steps; \square , 128 steps. One should notice the peculiar at first sight fact that $-\Delta S^p_{RS}$ first increases with an increasing number of steps N , up to about 58 steps, and then decreases with increasing N . (See text.)

show possible practical applications of this statistics. In particular, it has been suggested³³ that when the dimensions of the confining volume are of the same order of magnitude or less than those of the confined chains in its free state (B_0

**Figure 3.** Same plot as in Figure 2, to show how for a large number of steps N and small reduced edge length B_0 of the confining cube, all curves for the entropy change upon confinement for SAWs obeying reflecting statistics converge to nearly the same curve.**Figure 4.** Entropy change per lattice site $-\Delta S^p_{RS}$ due to confinement, for random-flight walks in reflecting statistics, for various chain lengths, as a function of the reduced edge length B_0 of the confining cube: \circ , 18 steps; \times , 38 steps; $+$, 58 steps; \bullet , 98 steps. Unlike what happens for self-avoiding walks, here $-\Delta S^p_{RS}$ steadily increases with an increasing number of steps N .

< 1), then a shift in statistics from absorbing to reflecting may gradually occur, in the range of B_0 from two to one. What prompted that suggestion is the fact that in such cases of severe confinement, the step-concentration profiles in AS and in RS are entirely different: in AS, almost all chain steps will concentrate in the central part of the available volume, leaving the region near the boundary almost step-free,^{29a} and

Table 5. Same Mean Parameters $\langle v \rangle$ and $\langle v \ln v \rangle$ as in Table 3, for Random-Flight Walks

$N = 18$			$N = 38$		
B	$\langle v \rangle$	$\langle v \ln v \rangle$	B	$\langle v \rangle$	$\langle v \ln v \rangle$
∞	1.00	0.00	∞	1.00	0.00
16	1.40×10	6.10×10	23	2.61×10^2	2.67×10^3
13	1.87×10	8.67×10	19	4.20×10^2	4.42×10^3
11	2.63×10	1.29×10^2	14	1.14×10^3	1.31×10^4
9	4.23×10	2.23×10^2	11	2.01×10^3	2.25×10^4
8	5.91×10	3.26×10^2	9	4.71×10^3	5.60×10^4
7	9.14×10	5.32×10^2	8	7.61×10^3	9.32×10^4
6	1.45×10^2	8.94×10^2	7	1.62×10^4	2.07×10^5
5	3.49×10^2	2.34×10^3	6	4.06×10^4	5.26×10^5
4	1.89×10^3	1.52×10^4	5	2.34×10^5	3.34×10^6

$N = 58$			$N = 98$		
B	$\langle v \rangle$	$\langle v \ln v \rangle$	B	$\langle v \rangle$	$\langle v \ln v \rangle$
∞	1.00	0.00	∞	1.00	0.00
35	4.87×10^3	7.33×10^4	35	2.60×10^6	6.05×10^7
29	4.87×10^3	7.36×10^3	27	9.31×10^7	2.72×10^9
19	4.92×10^3	7.40×10^4	18	4.36×10^7	1.16×10^9
15	4.08×10^4	6.60×10^5	15	3.70×10^8	1.10×10^{10}
11	1.06×10^5	1.81×10^6	11	8.45×10^8	2.39×10^{10}
9	4.48×10^5	8.14×10^6	9	3.97×10^9	1.17×10^{11}
8	9.73×10^5	1.81×10^7	8	9.17×10^9	2.70×10^{11}
7	2.45×10^6	4.65×10^7	7	6.54×10^{10}	2.06×10^{12}
6	1.31×10^7	2.70×10^8	6	8.38×10^{11}	2.82×10^{13}
5	1.45×10^8	3.16×10^9			

this effect becomes more and more pronounced as B_0 is further reduced. In RS, on the other hand, the concentration profile remains flat, whatever the respective dimensions of the free chain and of the confining volume.^{23,33} From the practical standpoint of polymer science, the AS profile looks unphysical, especially for polymer chains dissolved in good solvents. (This can occur, e.g., in microemulsions, when polymer chains are dissolved in microdroplets). One does not see why, in case of severe confinement, almost all chain-steps should concentrate inside a quite small volume in the central part of the available volume. This defies the effect of osmotic pressure (in the case of good solvents) and, more generally, the natural tendency of molecules to occupy all available space. However, if a shift of statistics from AS to RS occurs in the above indicated range, the step-concentration profiles will remain essentially flat, whatever B_0 , as MC simulations show. This particular property of RS statistics is qualitatively explained by considering the $v_j = w_j^{-1}$ parameter (eq 5): configurations wandering in the vicinity of the boundary will in the mean have fewer available directions for continuing being generated than those far away from the boundary, to the effect that v_j will display larger values for the former configurations. In other words, computer generated configurations will be mostly of the “near the boundary” kind, and it is this multiplication effect that is responsible for the flattening of chain-segment concentration profiles found in RS. Now consider a polymer chain *severely* confined inside some microdroplet, the solvent not being a bad solvent. Due to thermal motion, the polymer will tend to acquire any of all configurations in configurational space, being prevented to do this by the microdroplet’s boundary. The consequence will be that the configurations the chain will take will mostly be in close contact with the boundary. Only rarely, if ever, will the configurations taken by the chain be such as to have no or few contacts with the microdroplet’s surface. (We emphasize the boundary is supposed to be neutral with respect to chain-elements, neither

attractive nor repulsive.) This clearly means that here we have a thermodynamic multiplication of the occurrence of the first kind of configurations, to be put in parallel to the analogous (if not identical) multiplication effect occurring for computer generated chains in the RR procedure.

Another argument in support of the above argument follows from de Gennes’ concept of the chain being divided into independent “blobs” when one is in the semidilute concentration range.⁴² The semidilute concentration threshold c^* is defined as the concentration at which chains dissolved in a good solvent are “in contact” (but do not yet overlap). More precisely, $c^* = a^{-3}N^{-4/5}$, where a is the length of the statistical step. According to the scaling arguments developed by de Gennes, the correlation length ζ inside a specific chain for polymers dissolved in good solvents is proportional to $c^{-0.75}$. Neutron static (= equilibrium) scattering experiments^{43,44} are in support of this exponent. In the case of dynamic experiments, e.g., ultracentrifugation experiments, the situation is somewhat more complex. At any rate, it is quite certain that the correlation length significantly decrease when the concentration is increased. The above de Gennes scaling arguments hold for solutions of free chains in good solvents but will be adapted below to a single chain which is severely confined. Suppose now that the N -step chain is divided in spherical domains (or blobs) of radius ζ . Simple scaling calculations⁴² then show that the number n of Kuhn’s statistical elements inside each blob is proportional to $c^{-5/4}$, so that the total number of blobs along the chain is proportional to $N/n = Nc^{5/4}$, and thus increases with concentration. Now each blob may be considered to be an ideal statistical unit. This means that the angle between three contiguous blobs along the chain is arbitrary and that the mean distance between two blobs far apart along the chain is $\langle r \rangle = \zeta K^{1/2}$, if $K - 1$ is the number of intermediate blobs lying in between the two considered blobs.

Consider now that an N -step chain of mean free dimensions equal to $\langle r^2 \rangle^{1/2} = r_0$ is confined inside a microdroplet of radius $R < r_0$. The correlation length along the chain is necessarily less than R . But we can go further and assume (this is in fact quite realistic) that the mean concentration inside the droplet, proportional to N/R^3 , lies within the semidilute range. The confined chain can now be divided into blobs of radius $\zeta \sim c^{-0.75}$. The difference with the free case lies here in the fact that now the positions of two distant blobs along the chain are spatially uncorrelated, as soon as $\zeta K^{1/2}$ exceeds the radius R of the microdroplet. To a good approximation, the image that thus emerges is that of blobs of radius $\zeta < R$ that move essentially independently of each other inside the microdroplet. This means that the mean overall density of chain-steps inside the droplet will be constant, except perhaps at a distance $\zeta \ll R$ from the surface, if the concentration (i.e., the length N of the chain) is high enough. Thus, the concentration profile inside the microdroplet obtained using de Gennes’ blob approach is essentially a flat one, except perhaps at a distance ζ from the interface. As ζ decreases with increasing concentration (i.e., chain-length), the larger the confined chain the more the concentration profile will be flat, totally at variance with what would have been expected if usual AS did apply.

The conclusion to be drawn is that both thermodynamic considerations and the blob approach point to the fact that for severely confined chains usual AS should become

Table 6. Attrition in Reflecting Statistics for Free (Nonconfined) Self-Avoiding Walks and for Self-Avoiding Walks Confined inside Cubes of Reduced Edge Length Equal to Two^a

	N					
	18	38	58	78	98	128
$A(B_0 = \infty)$	1.0×10^{-4}	1.0×10^{-3}	3.6×10^{-3}	6.1×10^{-3}	8.9×10^{-3}	1.4×10^{-2}
$A(B_0 = 2)$	3.5×10^{-3}	1.0×10^{-2}	1.9×10^{-2}	2.5×10^{-2}	3.2×10^{-2}	4.3×10^{-2}
ΔA	3.4×10^{-3}	9.0×10^{-3}	1.5×10^{-2}	1.9×10^{-2}	2.3×10^{-2}	2.9×10^{-2}

^a The last line displays the difference between the two.

irrelevant. Of course, this does not prove that now RS applies instead. However, since RS provides flat concentration profiles, the idea deserves further consideration.

To the theorist, the essential argument against the use of RS in polymer solutions will be that it is a basic principle of statistical mechanics that in a thermodynamic ensemble all single available configurations should be weighted equally.⁴⁵ The answer to this basic argument is that discreet modeling of configurations on a lattice are not a one-to-one correspondence with real physical configurations. Rather, to each Monte Carlo configuration there corresponds a large but not necessarily constant number of physical configurations. Thus, Monte Carlo modeling corresponds to a "coarse graining" of physical phase space, and different weighting of MC configurations may be admitted if each Monte Carlo configuration does not correspond to an equal volume in physical phase space.

In experimental work, great care should be taken so that the condition of neutrality of the boundary (neither attractive nor repulsive) be as closely as possible respected. The authors are not aware of special experiments showing the step-concentration profiles of severely confined polymer chains, under the condition of neutral boundaries, and therefore closer examination of the suggestion of a change in statistics is not possible here. The problem addressed here is, of course, relevant to adsorption, e.g., in the case of polymers inside a slit whose width is small compared to the mean dimensions of the free polymer chains or for polymers in capillaries. However, for the time being, adsorption will rather be a nuisance for the purpose of the article, since it will obscure the basic simplicity of the problem addressed. It is a sine qua non condition, as stressed above, that the boundary be neutral with respect to the restricted or confined chains. No meaningful comparison or conclusion can otherwise be achieved.

Theoretical approaches of the adsorption problem are numerous,^{3-6,9,10,15,20,24} sometimes supported by MC simulations. Experimental concentration profiles, on the other hand, seem to be sparse, so that comparison of theoretical approaches with experiment is difficult. The same holds for the experimental verification of the suggestion made in the present section. Nevertheless, as an illustration of the effect of a possible change in statistics upon severe confinement, a brief discussion of the case of microemulsions is given here. The thermodynamic stability of a microemulsion is a function of the surface tension of the microdroplets in the microemulsion, and this in turn depends on various factors, including the pressure exerted by the confined chains on the microdroplet boundary. Figure 5 displays ΔS^p , the entropy change per lattice site due to confinement, in AS and in RS, for chains of 58 and 98 steps, as a function of the reduced cube edge length B_0 (for small B_0 values, which is the range of interest). The pressure exerted by the chain is pro-

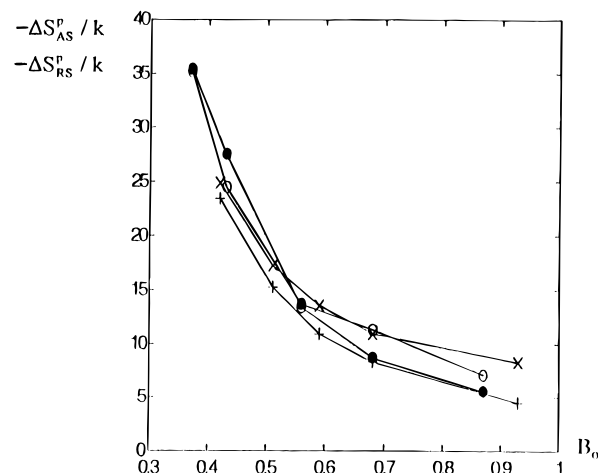


Figure 5. Entropy change per lattice site $-\Delta S^p$ due to confinement for self-avoiding walks, in absorbing and in reflecting statistics, for small values of the reduced edge length B_0 of the confining cubes: +, 58 steps, absorbing statistics; ●, 98 steps, absorbing statistics; x, 58 steps, reflecting statistics; ○, 98 steps, reflecting statistics. It is seen that as B_0 is reduced to very low values, all curves aggregate to a single curve. (See also Figure 1.)

portional, according to the statistics considered, to the slope of the S_{AS}^p/k and S_{RS}^p/k versus B_0 curves. For fixed B_0 , the slope of the curves S_{AS}^p/k and $\Delta S_{AS}^p/k$ and S_{RS}^p/k and $\Delta S_{RS}^p/k$, respectively, differ by the same amount. Therefore, qualitatively, the slope difference between AS and RS may be inferred from Figure 5. It is seen that the slope and thus the pressure is always less in RS. (This is also seen from Figure 1.) In other words, RS favors the stability of microemulsions. This pressure, of course, is only the purely entropic in origin pressure. The true pressure should take into account the solvent quality and adsorption phenomena. However, the fact remains that a change in statistics will be followed by a change in pressure. Analogous considerations would apply in all instances where macromolecular species find themselves severely confined.

V. CONCLUSION

The entropy problem of the random walker on a grid or lattice in reflecting statistics has been addressed using Monte Carlo simulations. The grid may be bounded or unbounded. In the case of the existence of a boundary, it was found that the entropy change from the unbounded state does not follow the same pattern for self-avoiding walks (SAWs, the walk cannot cross a previous path) and for random-flight walks (RFWs, there is no excluded volume, the walk can freely cross itself). In the former case, if the dimensions of the boundary are expressed in reduced coordinates, the entropy change first increases with the number N of steps in the walk and then decreases, while in the latter case the entropy change is a monotonously increasing function of the number N of

steps. This peculiar behavior of SAWs has been explained as being due to a “trapping” effect. On the other hand, in the case of severe confinement, all entropy changes tend to aggregate to a single curve. In the Discussion, it is further shown, through two distinct arguments, that usual absorbing statistics should not hold in the case of severe confinement, and possibly then reflecting statistics would apply instead. Definite proof one way or the other can only come through carefully designed special experiments, since usual experiments do not comply to the sine qua non condition that the boundary should be energetically neutral with respect to the walker’s steps (chain-elements). More generally, though this paper is primarily concerned with the Monte Carlo solution of a combinatorial problem and not particularly oriented to practical applications, it appears as probable that reflecting statistics may find applications in various fields of statistical analysis.

ACKNOWLEDGMENT

The authors thank Professor M. J. M. Abadie, LEMP/MAO, Université Montpellier II, Montpellier, France, for providing the means to perform the Monte Carlo computations of this work.

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CI960138U