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Statistics of confined self-avoiding walks. Part I: chain dimensions and concentration profiles

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Abstract. Self-avoiding (SAWs) and random-flight (RFWs) walks of varying number N of steps have been generated inside spheres of varying diameter R, using a random number generator and an *ad hoc* computer program. The Monte Carlo samples, usually of 100 000 walks, thus obtained, allowed the determination of the following ratios, as a function of N and R: first, the ratio $A = \langle r(N, R)\rangle / \langle r(N, \infty)\rangle$, where $\langle r(N, R)\rangle$ stands for the mean (in modulus) end-to-end distance of an N-step confined walk, and $\langle r(N, \infty)\rangle$ the same quantity for an N-step non-confined walk; also, the corresponding ratios B, C and D, for the root-mean-square end-to-end distance $\langle r^2\rangle^{1/2}$, the mean radius of gyration $\langle r_g\rangle$, and, finally, the root-mean-square radius of gyration $\langle r_g^2\rangle^{1/2}$. If reduced lengths are used, where the reduction length is of the form N^{ν}, ν being a scaling exponent, it is found that scaling, i.e. independence of the above ratios with respect to the step number in the walk, is well obeyed. The scaling exponent is equal to 0.592 for SAWs and to 0.500 for RFWs.

In order to determine the concentration profiles of end, mid- and overall steps inside the sphere, the last has been divided in a prescribed number of spherical shells, up to 22, of the same thickness, and the number of steps falling inside each shell registered. Again using reduced lengths, it was thus found that all concentration profiles obey scaling, that is, the concentration profile as a function of the reduced distance from the centre of the sphere is defined through a single curve, whatever the value of N. Our results allow a comparison of the parameters for confined SAWs and RFWs.

1. Introduction

In this paper we present a detailed analysis of the statistics of self-avoiding walks (SAWs) confined inside spheres of varying diameter. The incentive for studying this topic originates, of course, in that polymer chains in pores, a problem relevant to gel permeation chromatography (GPC) can be modelled by SAWs confined by boundaries of spherical or other shape. However, the present paper should primarily be considered as a study in its own right of the statistics of confined SAWs, independently of any correlation with real polymer chains confined inside pores.

General scaling arguments related to free or confined chains have been given by de Gennes [1]. Previous theoretical, exact enumeration (EE) and Monte Carlo (MC) studies of random-flight walks (RFWs) or SAWs confined inside various geometries are numerous [2–22]. These publications do not include papers more specifically concerned with adsorption phenomena or theta point polymer chain statistics. Despite this, it appears that, from the viewpoint of basic statistical features, several properties have not been studied, or, at least, properly elucidated. This statement is particularly true with respect

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to SAWs. More specifically, for SAWs confined inside a sphere, one can make reference to the following properties: (*a*) the mean and mean-square end-to-end distances and radii of gyration, as a function of the radius R of the confining sphere and the number N of steps in the walk; (*b*) the distribution of end and mid-steps of confined SAWs, as a function of r, the distance from the centre of the sphere, N and R; (*c*) the concentration profile of steps as a function of r, N and R; and (*d*) the entropy change upon confinement of the walk.

For RFWs, points (*b*), (*c*) and (*d*) above have been addressed analytically by Edwards and Freed [3] and by Collins and Wragg [4]. To our knowledge, no such equivalent treatment has been proposed for SAWs, and possibly the problem is not amenable to rigorous analytical treatment. Hence, the interest of addressing these topics and also additional ones using MC simulations. Here, in part I of the present study, points (*a*), (*b*) and (*c*) above will be addressed. Point (*d*) and related topics are left to a forthcoming paper.

Statistical samples of N-step SAWs embedded in the simple cubic lattice and confined by spheres of varying radius R were computer generated. Two sample generation procedures were used. These are now described in detail.

2. Chain generation processes—absorbing and reflecting statistics

Computer generation of walks, whether SAWs or RFWs, may be performed on- or off-lattice. Here we shall be exclusively concerned with SAWs and RFWs generated on the simple cubic lattice. The basic generation processes of SAWs in general (on- or off-lattice SAWs) are essentially two.

In a first-generation procedure [23, 24], considering first free (non-confined) walks, the SAWs are generated step by step, using a random number generator, and all configurations which display lattice points twice visited by steps are eliminated from the statistics. In practice, the chain generation process is stopped as soon as the walk being generated encounters an already visited lattice point, and a new chain is initiated until a chain is obtained which is devoid of any double occupancy. By this procedure, in order to define mean values, all chains in the sample have the same statistical weight. This advantage is, however, counterbalanced by *attrition*: as soon as the number of steps N in the walk becomes large enough, the attrition (i.e. the probability of failure when initiating a chain) becomes close to one, and, correspondingly, the yield close to zero. This procedure, pionneered by Wall and his coworkers [23, 24], we call the *absorbing chain generation procedure*, and the resulting statistics *absorbing statistics* (AS). The attrition, a function of the number N of steps in the walk, will be denoted by the symbol A.

In a second-generation procedure, initiated by Rosenbluth and Rosenbluth [25], the walk is not stopped when it encounters an already visited lattice point. Instead, another direction with no such effect is sought. If there are k such directions, one of these is then taken with probability k^{-1}. In practice, the computer screens for possible directions one or more steps ahead, and chooses with equal probability one of these possible directions. Thus, an initiated chain is always terminated (no attrition), unless the chain goes through a nest. In such a case, the walk is eliminated, and a new walk is initiated. This generation procedure we call the *reflecting chain generation procedure*, and the corresponding statistics *reflecting statistics* (RS). In RS, the configurations

obtained do not occur with the same probability. Compact configurations (i.e. configurations where many neighbour sites of a given step are occupied by other steps) are favoured. For this reason, any configuration obtained must be weighed by a proper statistical weight, in order to revert to the equal probability of configurations of absorbing statistics. Let us consider the jth SAW generated in the MC sample of N-step SAWs and let us introduce the quantity

$$w^j = 6^{n_6^j} \times 5^{n_5^j} \times 4^{n_4^j} \times 3^{n_3^j} \times 2^{n_2^j} \times 1^{n_1^j} / 6 \times 5^{N-1} = \prod_{i=1}^{6} (i)^{n_i^j} / Z_{\max} \tag{1a}$$

$$\sum n_i^j = N \tag{1b}$$

$$Z_{\max} = 6 \times 5^{N-1}. \tag{1c}$$

Here i stands for the number of possible choices for the direction to follow when generating the kth step of SAW j (up to five for all steps in the case of the simple cubic lattice, except the first one, for which there are six or less available directions, according to whether the first step lies on a lattice point far from or in the vicinity of the sphere surface); n_i^j is the number of occurrences of this number of choices for the whole walk when completed, where n_6^j takes the values one or zero. The statistical weight to be attributed to SAW j in the sample is then w^j [25–27]. Qualitatively, this means that a SAW, where, in the mean, many neighbouring lattice points of any steps are occupied by other steps of the SAW ('compact' SAWs) occur more often than necessary in the MC sample when reflecting statistics are used. The more 'compact' the configuration considered, the smaller the corresponding weighting factor w^j will then be. For a completely 'compact' SAW (=globule or else Hamiltonian walk on a lattice), w^j is of the order of $5^{(1-N)}$. The other limit of w^j is one, when there are no nearest neighbours between steps in the walk. Obviously, the weighting factor dereases in the mean as N increases. The mean value in a sample of S SAWs,

$$\langle W \rangle = S^{-1} \sum_{j=1}^{S} w_j \tag{2}$$

is a fundamental parameter in RS, as it will become clear in what follows. We shall refer to it as the *compactness* parameter.

The same parameters as above, i.e. the attrition A in AS and the parameter $\langle W \rangle$ in RS, also apply if now the walk, instead of being free in space, is constrained to lie inside the boundary defined by a sphere of radius R. In particular the attrition $A(N, R)$ in AS is enhanced by the presence of the boundary, since now any configuration crossing the surface of the sphere is eliminated from the statistics, even if the walk is otherwise a SAW. In what follows $A(N, \infty)$ stands for the attrition of free (unconfined) SAWs, while $A(N, R)$ stands for the attrition of walks confined inside a sphere of radius R. Analogously, dropping for simplicity the mean value brackets, we define in RS $W(N, \infty)$ and $W(N, R)$.

The concepts of attrition and compactness may also be applied to confined RFWs. For free RFWs, the attrition is zero and the compactness parameter equal to one.

For the purposes of the present study, no sample enrichment procedures have been considered. Only the two basic step-by-step generation procedures have been used, here designated by absorbing and reflecting procedures. These two basic procedures are variously named in the literature. Our particular designations of *absorbing* and *reflecting* present the advantage of being reminiscent of the physics of the generation process. Further, they are in accord with Smoluchowski's denominations, who was the first to

consider absorbing and reflecting barriers, when studying the physics of colloïd aggregation [28, 29]. To end this section let us point out that non-weighed RS, i.e. the statistics of the reflecting generation procedure, where all configurations in the sample are given the same statistical weight, may be of interest in its own right. This statistics, however, will not be considered here, the study being restricted to AS and the equivalent weighed RS (WRS).

3. The computer programs

The distinctive feature of our walk generation process is that the walks should lie inside spheres of radius R. To initialize a walk, three integer random numbers lying between zero and R are first obtained using a random number generation procedure. If the corresponding point, taking as the origin of Cartesian coordinates the centre of the sphere, corresponds to a lattice point within the sphere, the walk generation process is pursued, by instructing the random number generator to provide an integer lying between one and six, which will define the direction of the first step in the walk. Otherwise, a new set of three random numbers is sought. This procedure ensures the statistical independence of the three coordinates x, y and z, and a uniform distribution of starting points for all lattice points inside the sphere. For the second and all following steps in the walk, one of the six possible directions is excluded, that corresponding to the reverse walk. In AS, the walk is completed only if at no time does it go through an already occupied lattice point and at no time crosses the surface of the sphere. This means that, as N increases and (or) R decreases, the attrition $A(N, R)$ very rapidly becomes very close to one, and correspondingly the yield $1-A(N, R)$ close to zero. To circumvent this effect, RS has to be used instead. Here the number of random integers provided corresponds at each step being generated to the number of allowed directions for this step, this being determined by the previously generated steps in the walk and the surface of the sphere. Only if the walk goes inside a nest (no further possibility to pursue the walk generation process) is the walk abandoned, and a new walk initiated. Thus, in RS, the attrition is usually small, except if the dimensions of the confining sphere are of the same order of magnitude as those of the chain, or smaller. Most of our MC data have been obtained using the weighed reflecting procedure, the absorbing procedure having been used only in a limited number of instances, primarily in order to ensure that the results from both procedures are statistically indistinguishable.

In order to be able to specify the distribution of end and mid-points inside the sphere, as well as the concentration profile of steps, as functions of the distance r from the centre (points (*a*) to (*c*) in the introduction), the following refinement was introduced in the computer program: the sphere of radius R was divided into an arbitrary number (up to 22) of spherical shells of the same thickness. The number of, for example, end-points of SAWs in the MC sample, falling inside each spherical shell, was recorded by the computer, and this number divided by the number of lattice points within each shell, to ensure a consistent determination of concentration or density. The versatility of our program also permitted to initiate the walk generation process not uniformly inside the sphere, but only inside some (in particular only one) of the prescribed spherical shells. Thus, it is possible to specify the statistics of SAWs starting from the central or any other shell, and even only from the centre of the sphere. Further, it is also possible to attribute different weights to the lattice points in different shells for the

initialization procedure. In the present paper only the statistics of the uniform distribution of starting points will be reported (i.e. the basic case where all lattice points within the sphere have equal probability to be considered as starting points).

For completeness and in order to make a comparison available, RFWs have also been generated. The generation procedures are the same as previously, with the difference that double or multiple occupancy of a lattice site is not now forbidden. Thus, attrition here orginates only in the presence of a boundary, and similarly the compactness parameter W differs from one only because of this boundary, since near the surface of the sphere there are less than six possible directions to continue generating the random walk.

4. Monte Carlo results for chain dimensions and concentration profiles

In this paper we give results for the mean chain dimensions and concentration profiles of confined chains, as functions of the number N of steps in the chain and the radius R of the confining sphere. The number of configurations of confined SAWs and related problems, especially the entropy problem, will be dealt with in a forthcoming paper.

Since most of our MC data have been obtained using WRS, we give the definitions of the various mean quantities we used for this statistics below. The corresponding definitions for AS are obtained by letting all w^j in the equations below equal unity:

$$\langle r\rangle = \frac{\sum_{j=1}^{S} w^j r^j}{\sum_{j=1}^{S} w^j} \tag{3}$$

$$\langle r^2\rangle = \frac{\sum_{j=1}^{S} w^j (r^j)^2}{\sum_{j=1}^{S} w^j} \tag{4}$$

$$\langle r_g\rangle = \frac{\sum_{j=1}^{S} w^j r_g^j}{\sum_{j=1}^{S} w^j} \tag{5}$$

$$\langle r_g^2\rangle = \frac{\sum_{j=1}^{S} w^j (r_g^j)^2}{\sum_{j=1}^{S} w^j}. \tag{6}$$

In the above relationships, r^j is the end-to-end distance (in modulus) of walk j, and r_g^j the corresponding radius of gyration. S is the sample magnitude.

From the onset, it may be convenient to express all data using reduced variables $\rho_0 = R/\langle r(\infty)\rangle_N$ and $\rho = r/\langle r(\infty)\rangle_N$, where R is the radius of the confining sphere, r the distance from the centre of the sphere, and $\langle r(\infty)\rangle_N$ the mean end-to-end distance of N step walks in free space. In this way, scaling, that is, properties which depend on ρ_0 and ρ but not on N, will become apparent at once. Of course, instead of using $\langle r(\infty)\rangle$ as reduction parameter, one could have just as well used $\langle r^2(\infty)\rangle^{1/2}$, or the mean or root-mean-square radius of gyration. All these quantities are essentially equivalent, as for large enough N (say, $N>20$) they all obey, to a good approximation, a simple law of the form

$$\langle x(\infty)\rangle = a_x N^{\nu} \tag{7}$$

where ν is a scaling exponent (critical exponent for the correlation length) and a_x a prefactor relevant to the mean quantity $\langle x(\infty)\rangle$. Equation (7) has been established in the earliest days of simulations on SAWs [23, 24], and the fact that it now appears to strictly correct only in the limit of very large N (otherwise one has to take into account

'correction to scaling' exponents) is irrelevant for present purposes. In three dimensions, in the range $20 < N < 10^4$, it is convenient to use the MC value $\nu_{MC} = 0.592$, which has been found by numerous investigators [30], instead of the renormalization group value $\nu_{RG} = 0.588$, which, though in fact the correct one, is convenient only in the limit of very large N [31].

Table 1. $A = \langle r(\rho_0)\rangle / \langle r(\infty)\rangle$, $B = \langle r^2(\rho_0)\rangle^{1/2} / \langle r^2(\infty)\rangle^{1/2}$, $C = \langle r_g(\rho_0)\rangle / \langle r_g(\infty)\rangle$ and $D = \langle r_g^2(\rho_0)\rangle^{1/2} / \langle r_g^2(\infty)\rangle^{1/2}$, where $\langle r\rangle$ stands for the mean end-to-end distance and $\langle r_g\rangle$ for the mean radius of gyration, as a function of the reduced radius ρ_0 of the confining sphere, $\rho_0 = R/\langle r\rangle$, for SAWs. MC results from 18 to 58 steps using AS. MC sample sizes are of 100 000 independent (=non-correlated) walks, for all the data here reported. The error is estimated to be ±0.006.

ρ_0	A	B	C	D
18 steps				
$\langle r(\infty)\rangle = 5.52$		$\langle r^2(\infty)\rangle^{1/2} = 5.84$		
$\langle r_g(\infty)\rangle = 2.30$		$\langle r_g^2(\infty)\rangle^{1/2} = 2.33$		
4.0	0.987	0.987	0.991	0.992
3.0	0.980	0.980	0.987	0.988
2.0	0.964	0.964	0.978	0.979
1.5	0.940	0.941	0.965	0.964
1.0	0.868	0.868	0.922	0.924
28 steps				
$\langle r(\infty)\rangle = 7.18$		$\langle r^2(\infty)\rangle^{1/2} = 7.62$		
$\langle r_g(\infty)\rangle = 2.98$		$\langle r_g^2(\infty)\rangle^{1/2} = 3.03$		
4.0	0.985	0.984	0.993	0.991
3.0	0.978	0.977	0.987	0.986
2.0	0.960	0.960	0.977	0.976
1.5	0.933	0.934	0.960	0.960
1.0	0.851	0.851	0.916	0.911
38 steps				
$\langle r(\infty)\rangle = 8.63$		$\langle r^2(\infty)\rangle^{1/2} = 9.16$		
$\langle r_g(\infty)\rangle = 3.58$		$\langle r_g^2(\infty)\rangle^{1/2} = 3.64$		
4.0	0.983	0.984	0.989	0.990
3.0	0.975	0.976	0.983	0.985
2.0	0.955	0.957	0.972	0.973
1.5	0.930	0.932	0.958	0.958
1.0	0.845	0.845	0.908	0.906

Table 1 displays the values of $A = \langle r(\rho_0)\rangle / \langle r(\infty)\rangle$, the mean end-to-end distance for the reduced value ρ_0 of the confining sphere radius over the mean end-to-end distance of the free walk, $B = \langle r^2(\rho_0)\rangle^{1/2} / \langle r^2(\infty)\rangle^{1/2}$, the same ratio for the root-mean-square end-to-end distance, $C = \langle r_g(\rho_0)\rangle / \langle r_g(\infty)\rangle$, the same ratio for the radius of gyration, and finally $D = \langle r_g^2(\rho_0)\rangle^{1/2} / \langle r_g^2(\infty)\rangle^{1/2}$, the same ratio for the root-mean-square radius of gyration, for N-values ranging from 18 to 58 steps. These quantities have been determined in this table using AS (see section 2). In table 2 the same quantities have been determined using WRS, to ensure that both walk generation procedures lead statistically to the same mean values. Because of the very fast increase in computational time when using AS, one cannot reach low ρ_0 values with this generation procedure. However, the ρ_0 values accessible by AS are sufficient to show that there is no discrepancy between the two procedures, as comparison of the data in tables 1 and 2 shows. Also shown in table 2 are the corresponding quantities for RFWs of the same number of

Table 2. A, B, C and D, as defined in table 1, as functions of ρ_0, the reduced radius of the confining sphere. MC results for SAWs from WRS. Also shown are the results for random-flight statistics (RFS). For SAWs, there is good agreement with the results of table 1, that is, AS and WRS are equivalent and may be used interchangeably. Table 2 also shows that scaling, that is, independence of the parameters with respect to the number of steps N in the walk, is well obeyed, except for the shortest walk of 18 steps and the smallest values of ρ_0. It should be remarked that for not confined (free) RFS, the theoretical value $6^{1/2} = 2.4495$ for the ratio B/D is not yet attained for 58 steps, while in WRS a limiting value of the order of 2.51 for the above ratio is already attained for as few as 18 steps. Complementary simulations, not reported here, have shown that for RFS the ratio increases slowly with N, to be within 0.005 of the theoretical limiting value for 250 steps. No explanation is offered for this difference in behaviour between SAWs and RFWs, which seems to be reported here for the first time. The error is estimated to be ±0.006.

	AS-WRS				RFS			
ρ_0	A	B	C	D	A	B	C	D
18 steps								
$\langle r(\infty)\rangle = 5.52$		$\langle r^2(\infty)\rangle^{1/2} = 5.84$			$\langle r(\infty)\rangle = 3.92$		$\langle r^2(\infty)\rangle^{1/2} = 4.24$	
$\langle r_g(\infty)\rangle = 2.30$		$\langle r_g^2(\infty)\rangle^{1/2} = 2.33$			$\langle r_g(\infty)\rangle = 1.73$		$\langle r_g^2(\infty)\rangle^{1/2} = 1.78$	
4.0	0.987	0.987	0.991	0.994	0.973	0.975	0.984	0.981
3.0	0.980	0.980	0.987	0.990	0.964	0.967	0.978	0.975
2.0	0.964	0.964	0.978	0.980	0.934	0.937	0.959	0.956
1.5	0.936	0.938	0.963	0.964	0.895	0.897	0.935	0.930
1.0	0.869	0.869	0.925	0.925	0.785	0.784	0.866	0.857
0.8	0.777	0.775	0.874	0.871	0.680	0.676	0.798	0.786
0.6	0.607	0.605	0.778	0.771	0.546	0.545	0.690	0.676
0.4	0.394	0.388	0.593	0.586	0.379	0.389	0.555	0.541
28 steps								
$\langle r(\infty)\rangle = 7.18$		$\langle r^2(\infty)\rangle^{1/2} = 7.62$			$\langle r(\infty)\rangle = 4.88$		$\langle r^2(\infty)\rangle^{1/2} = 5.29$	
$\langle r_g(\infty)\rangle = 2.98$		$\langle r_g^2(\infty)\rangle^{1/2} = 3.03$			$\langle r_g(\infty)\rangle = 2.14$		$\langle r_g^2(\infty)\rangle^{1/2} = 2.20$	
4.0	0.985	0.985	0.991	0.991	0.973	0.974	0.982	0.981
3.0	0.978	0.978	0.988	0.988	0.961	0.962	0.973	0.972
2.0	0.961	0.961	0.977	0.976	0.934	0.935	0.955	0.972
1.5	0.936	0.936	0.963	0.962	0.893	0.893	0.929	0.925
1.0	0.853	0.852	0.916	0.913	0.772	0.768	0.851	0.844
0.8	0.753	0.750	0.859	0.853	0.683	0.677	0.791	0.781
0.6	0.609	0.605	0.772	0.762	0.517	0.512	0.665	0.652
0.4	0.418	0.414	0.615	0.606	0.355	0.355	0.527	0.515
38 steps								
$\langle r(\infty)\rangle = 8.63$		$\langle r^2(\infty)\rangle^{1/2} = 9.16$			$\langle r(\infty)\rangle = 5.68$		$\langle r^2(\infty)\rangle^{1/2} = 6.16$	
$\langle r_g(\infty)\rangle = 3.58$		$\langle r_g^2(\infty)\rangle^{1/2} = 3.64$			$\langle r_g(\infty)\rangle = 2.48$		$\langle r_g^2(\infty)\rangle^{1/2} = 2.55$	
4.0	0.982	0.983	0.989	0.989	0.974	0.974	0.981	0.981
3.0	0.977	0.978	0.986	0.987	0.964	0.964	0.974	0.974
2.0	0.951	0.953	0.972	0.972	0.935	0.936	0.955	0.954
1.5	0.930	0.931	0.958	0.957	0.890	0.889	0.927	0.924
1.0	0.849	0.849	0.910	0.908	0.772	0.768	0.849	0.841
0.8	0.751	0.749	0.852	0.848	0.670	0.664	0.779	0.768
0.6	0.603	0.599	0.760	0.753	0.536	0.530	0.677	0.664
0.4	0.414	0.410	0.609	0.600	0.377	0.377	0.522	0.510

Table 2. (Continued)

	AS-WRS				RFS			
ρ_0	*A*	*B*	*C*	*D*	*A*	*B*	*C*	*D*
48 steps								
$\langle r(\infty)\rangle = 9.89$		$\langle r^2(\infty)\rangle^{1/2} = 10.51$			$\langle r(\infty)\rangle = 6.39$		$\langle r^2(\infty)\rangle^{1/2} = 6.93$	
$\langle r_g(\infty)\rangle = 4.10$		$\langle r_g^2(\infty)\rangle^{1/2} = 4.18$			$\langle r_g(\infty)\rangle = 2.78$		$\langle r_g^2(\infty)\rangle^{1/2} = 2.86$	
4.0	0.989	0.989	0.992	0.991	0.972	0.974	0.981	0.981
3.0	0.973	0.973	0.985	0.983	0.961	0.961	0.973	0.973
2.0	0.961	0.962	0.977	0.975	0.931	0.932	0.953	0.952
1.5	0.930	0.931	0.958	0.956	0.891	0.891	0.927	0.923
1.0	0.840	0.840	0.907	0.903	0.765	0.760	0.844	0.836
0.8	0.750	0.748	0.856	0.858	0.677	0.670	0.783	0.773
0.6	0.602	0.597	0.761	0.752	0.538	0.532	0.680	0.667
0.4	0.409	0.406	0.606	0.595	0.382	0.337	0.532	0.519
58 steps								
$\langle r(\infty)\rangle = 11.06$		$\langle r^2(\infty)\rangle^{1/2} = 11.78$			$\langle r(\infty)\rangle = 7.02$		$\langle r^2(\infty)\rangle^{1/2} = 7.62$	
$\langle r_g(\infty)\rangle = 4.60$		$\langle r_g^2(\infty)\rangle^{1/2} = 4.68$			$\langle r_g(\infty)\rangle = 3.05$		$\langle r_g^2(\infty)\rangle^{1/2} = 3.14$	
4.0	0.980	0.980	0.985	0.986	0.974	0.974	0.981	0.981
3.0	0.979	0.978	0.987	0.987	0.961	0.961	0.973	0.973
2.0	0.957	0.956	0.972	0.972	0.930	0.930	0.953	0.952
1.5	0.924	0.925	0.956	0.955	0.889	0.889	0.926	0.923
1.0	0.841	0.840	0.904	0.901	0.776	0.761	0.845	0.837
0.8	0.746	0.742	0.852	0.846	0.667	0.659	0.776	0.765
0.6	0.591	0.588	0.755	0.746	0.517	0.511	0.660	0.647
0.4	0.403	0.399	0.597	0.588	0.343	0.340	0.493	0.480

steps. Tables 1 and 2 convincingly show that scaling is well obeyed for all the above mean quantities. It is then convenient to express the inverse mean values A^{-1}, B^{-1}, C^{-1} and D^{-1} in increasing powers of ρ_0^{-1}, so that at the limit of an infinite radius of the confining sphere, the value one, corresponding to free walks, is recovered:

$$A^{-1} = 1 + a_1\rho_0^{-1} + a_2\rho_0^{-2} + a_3\rho_0^{-3} + a_4\rho_0^{-4}. \tag{8}$$

The a_i values for the various means are given in table 3. This table has been obtained using the data in table 2 and a least squares fit algorithm.

In figures 1 and 2 are displayed the concentration profiles of end steps *E* and mid-steps *F* of the SAWs as functions of *N*, of the reduced radius ρ_0 of the sphere, and of the reduced distance ρ from its centre. It is seen that scaling, i.e. independence of these quantities with respect to *N* when reduced-length variables are used, is satisfactory, except for the lowest *N*- and ρ-values. Therefore, one may look, for not too small *N*- and ρ-values, for an expansion in powers of ρ ($0 < \rho < \rho_0$), where the prefactors α, β, γ and δ are functions of ρ_0:

$$E(\rho_0, \rho) = \alpha(\rho_0) + \beta(\rho_0)\rho + \gamma(\rho_0)\rho^2 + \delta(\rho_0)\rho^3 + \ldots. \tag{9}$$

An equivalent expansion holds for *F*. The functions $\alpha(\rho_0)$, etc, may be visualized by plotting the α-values as a function of ρ_0, the reduced radius of the sphere (figure 3). An expansion of the form (9) is the condensation in a single relationship of the information contained in all possible figures of the kind displayed in figures 1 and 2. Our MC data are not, however, quantitatively dense enough and qualitatively precise enough to assign

Table 3. Prefactors of the expansions for the parameters A^{-1}, B^{-1}, C^{-1} and D^{-1}, defined in table 1, in powers of ρ_0^{-1}, where ρ_0 is the reduced radius of the confining sphere, for SAWs and RFWs (see equation (8)). The data of table 2 have been used. The last column displays the mean square error (MSE) in the fitting process. Such expansions are warranted by scaling, that is, independence of the above parameters with respect to the length of the walk.

	a_1	a_2	a_3	a_4	MSE $\times 10^{+3}$
WRS					
A^{-1}	0.11395	−0.22799	0.40031	−0.09318	9.910
B^{-1}	0.11365	−0.22930	0.40666	−0.09515	9.488
C^{-1}	0.04732	−0.03451	0.12221	−0.02896	4.858
D^{-1}	0.04326	−0.02706	0.12401	−0.02989	4.266
RFS					
A^{-1}	0.11818	−0.11052	0.38191	−0.09362	10.024
B^{-1}	0.08324	−0.00223	0.31167	−0.07995	7.825
C^{-1}	0.05605	0.03069	0.12932	−0.03391	3.735
D^{-1}	0.04765	0.05545	0.12404	−0.03382	4.949

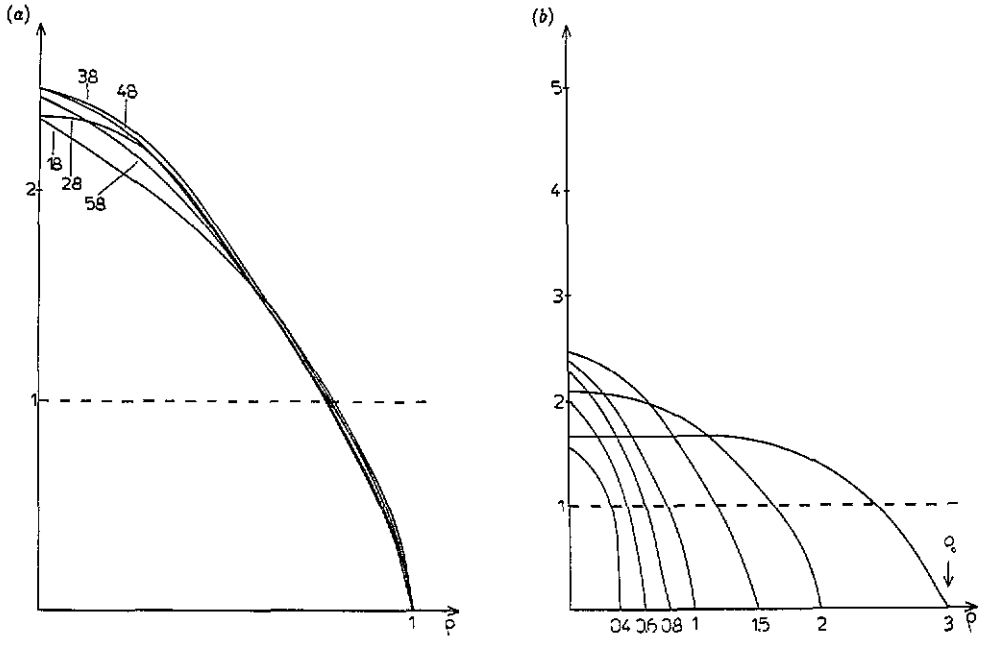

Figure 1. (*a*) SAW concentration of end steps, for ρ_0, the reduced radius of the confining sphere equal to one, and for values of N as indicated. Scaling, i.e. independence with respect to N, is well obeyed. (*b*) SAW concentration of end steps, for values of ρ_0 as indicated. Because of scaling, these curves do not depend on the value of N, the number of steps in the walk. The horizontal line corresponds to the uniform concentration within the sphere. To obtain the actual concentrations corresponding to each curve for a given sample size, one should multiply the ordinates by ρ_0^{-3}.

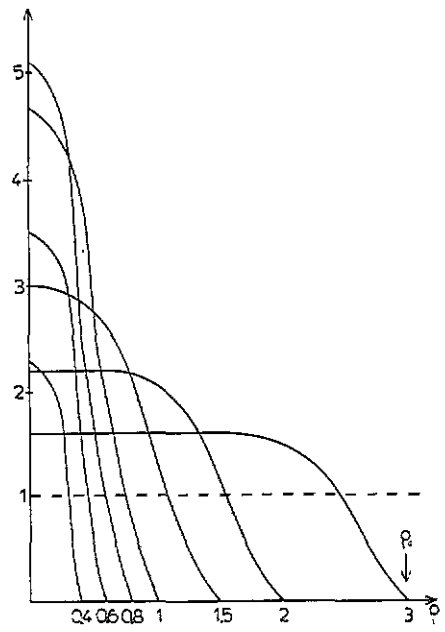

Figure 2. SAW concentration of mid-steps, as a function of ρ_0, the reduced radius of the confining sphere. The horizontal line corresponds to the uniform concentration within the sphere. To obtain the actual concentrations corresponding to each curve for a given sample size, one should multiply the ordinates by ρ_0^{-3}.

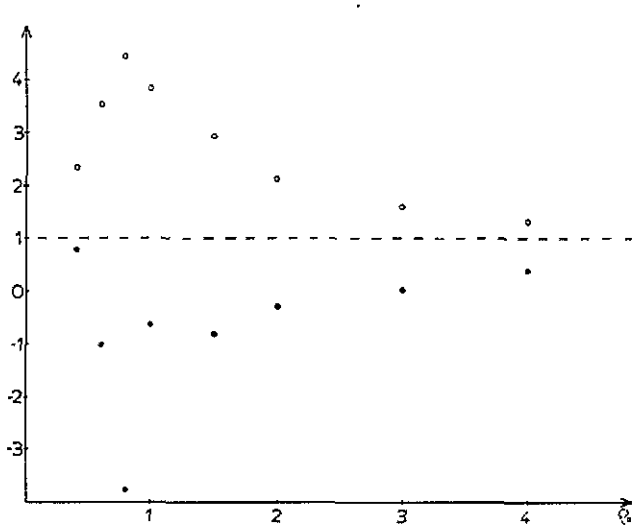

Figure 3. Variation of the prefactors $\alpha(\rho_0)$ (○) and $\beta(\rho_0)$ (●) for step concentration in the expansion of equation (9), as a function of the reduced radius ρ_0 of the confining sphere.

Table 4. Prefactors $\alpha(\rho_0)$, $\beta(\rho_0)$, $\gamma(\rho_0)$ and $\delta(\rho_0)$, where ρ_0 is the reduced radius of the confining sphere, in the expansion (9), for the density of end steps $E(\rho_0, \rho)$ and mid-steps $F(\rho_0, \rho)$, as functions of the reduced distance $(0<\rho<\rho_0)$ from the centre of the confining sphere. Scaling of the density profiles (see figure 1(*a*)), allows such an expansion.

$E(\rho_0, \rho)$	$\alpha(\rho_0)$	$\beta(\rho_0)$	$\gamma(\rho_0)$	$\delta(\rho_0)$	MSE $\times 10^{+2}$
ρ_0					
4	1.49699	−0.21066	0.20086	−0.05433	3.521
3	1.70527	−0.19739	0.31062	−0.14266	0.910
2	2.14206	−0.07372	−0.14657	−0.17372	2.876
1.5	2.46484	−0.15944	−0.94272	−0.00616	3.396
1.0	2.36452	−0.71960	−1.24288	−0.13348	4.911
0.8	2.29310	−1.07706	−0.85034	−1.29188	10.242
0.6	2.00655	−1.29246	0.61373	−6.05622	11.466
0.4	1.60318	−1.57910	7.85277	−28.37333	17.953

$F(\rho_0, \rho)$	$\alpha(\rho_0)$	$\beta(\rho_0)$	$\gamma(\rho_0)$	$\delta(\rho_0)$	$\varepsilon(\rho_0)$	MSE $\times 10^{+2}$
ρ_0						
4	1.35001	0.39807	−0.53797	0.27448	−0.04638	2.464
3	1.53275	0.41211	−0.79310	0.59217	−0.15018	1.302
2	2.37097	−1.21260	3.05485	−2.60021	0.50923	6.372
1.5	3.14686	−1.69919	6.25089	−10.02504	3.82474	8.172
1.0	4.40133	2.88603	−11.57372	−8.59143	13.81574	56.744
0.8	4.81322	3.91246	−12.56955	−46.81606	62.67413	135.571
0.6	3.48097	−1.02817	18.45764	−97.09703	83.18192	104.704
0.4	2.41664	−2.98805	23.82456	−68.51644	−54.15030	77.011

a definite analytical form to the functions $\alpha(\rho_0)$, $\beta(\rho_0)$ and even more so to the functions $\gamma(\rho_0)$ and $\delta(\rho_0)$. For this reason, we only tabulate in table 4, for the end steps E and the mid-steps F, the values of the above prefactors as functions of ρ_0.

In figure 4 the density G of steps as a function of N, ρ_0 and ρ is shown for SAWs. Again scaling is obeyed, with the same reservations as for the concentration of end and mid-steps. Table 5 displays the values of the prefactors α, β, γ and δ for segment concentration in an expansion analogous to the expansion (9) for end steps. As for end and mid-steps, the quantity and precision of our data does not permit to fix with certainty the analytical form of these prefactors as functions of ρ_0. Figure 5 displays the step density for RFWs, and to make the comparison with SAWs visible, figure 6 displays the profiles for both SAWs and RFWs, for a few values of ρ_0.

5. Discussion

As already indicated in the introduction, only features proper to AS are considered here. Also, the concentration profiles provided here correspond to the case where the confining boundary is a zero-infinite potential. In other words, adsorption phenomena are not taken into account, as they lie beyond the scope of the present paper. Finally, the statistics involve only the basic case where there are no energetic interactions between nearest neighbours, other than the geometric excluded volume constraint. For real polymer chains in solution, this corresponds approximately to chains dissolved in an athermal solvent.

From the theoretical standpoint, the concentration profiles of RFW chains confined inside a cubic box have been studied by Collins and Wragg [4]. To this end, they used

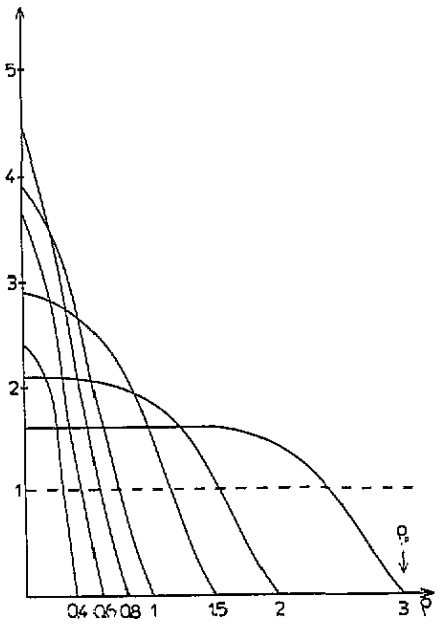

Figure 4. SAW concentration of steps as a function of ρ_0, the reduced radius of the confining sphere. The horizontal line corresponds to the uniform concentration within the confining sphere. Actual concentrations for each ρ_0 value are obtained by multiplying the corresponding ordinates by ρ_0^{-3}.

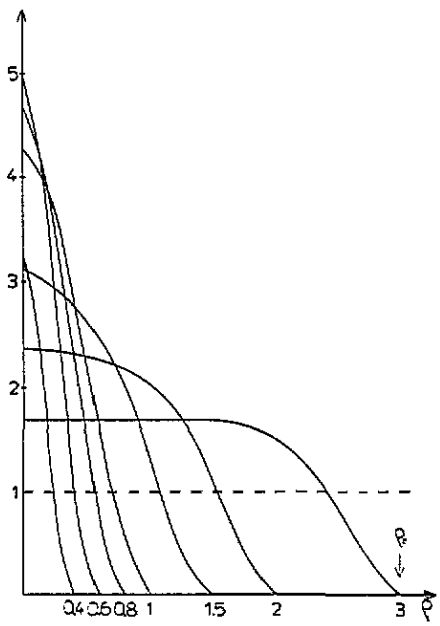

Figure 5. RFW concentration of steps as a function of ρ_0, the reduced radius of the confining sphere. The horizontal line corresponds to the uniform concentration of segments inside the sphere.

Table 5. Prefactors $\alpha(\rho_0)$, $\beta(\rho_0)$, $\gamma(\rho_0)$ and $\delta(\rho_0)$, in the expansion (9), for the density of segments, where ρ_0 is the reduced radius of the confining sphere and ρ $(0<\rho<\rho_0)$ the reduced distance from the centre of the sphere.

$G(\rho_0, \rho)$	$\alpha(\rho_0)$	$\beta(\rho_0)$	$\gamma(\rho_0)$	$\delta(\rho_0)$	$\varepsilon(\rho_0)$	MSE $\times 10^{+2}$
ρ_0						
4	1.31919	0.40292	−0.54758	0.28177	−0.04821	2.219
3	1.59755	0.03592	−0.13874	0.17847	−0.066954	1.058
2	2.12974	−0.27668	0.83293	−0.94605	0.14890	4.844
1.5	2.94295	−0.79975	1.73496	−3.65264	1.28504	5.170
1.0	3.83624	−0.61822	−4.62193	−4.12158	5.80414	7.366
0.8	4.44822	−3.75552	−3.05579	−6.90928	10.42646	9.935
0.6	3.56248	−1.00559	−14.45037	−4.49493	26.01675	13.237
0.4	2.33605	0.79250	−10.21466	−15.35651	−10.77303	9.428

a previous theoretical work by Edwards and Freed [3]. On the other hand, most MC or EE studies of confined chains, whether RFW or SAW, are concerned with chains inside strips or tubes, or limited by a wall [6–8, 11–16], which means that at least one dimension of the chain is allowed to go to infinity. An MC study of SAWs confined inside cubes has been performed by Cifra *et al* [19], but their work is primarily concerned with the entropy problem. The same may be said regarding the work of Casassa on confined RFWs inside various geometries [2], apparently the first theoretical work to appear on this topic. Akin but by no means identical to the problem of chains confined inside

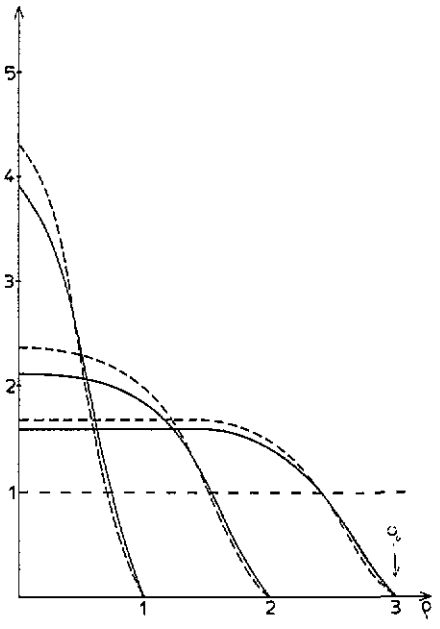

Figure 6. Comparison of step concentration profiles for RFWs (solid curve) and SAWs (broken curve), for several values of the reduced radius of the confining sphere. Notice that the reduction length is not the same for RFWs ($0.922N^{0.5}$) and SAWs ($N^{0.592}$), so that the same ρ_0 values correspond to different actual diameters of the confining spheres for RFWs and SAWs, respectively.

spheres is that of chains generated in spaces containing fixed obstacles [18, 32]. Detailed investigations of the concentration profiles of RFWs or SAWs confined inside spheres, except [17], are not known to the present authors. Therefore, comparison with previous work will be limited here to the theoretical work of Collins and Wragg, on RFW chains. The comparison will necessarily be qualitative, as the confining geometries are not identical.

Inspection of the figures given in the above reference shows that the plateau region for the concentration profiles of end and mid-steps disappears, in the present paper's notations, for $\rho_0 \approx 1.3$ (see figure 5 in [4]). The present investigation shows that the plateau region for the various concentration profiles disappears in the vicinity of $\rho_0 \approx 1.5$, in fair agreement with the previous value. More precise comparison is however not possible, because of the differing geometries of confinement, and the lack of more comprehensive data. From this we conclude that the presence of a boundary is not felt beyond approximately 1.5 times the mean end-to-end distance, a conclusion in accord with the less precise data of [17].

A point which should be stressed is that, for symmetry reasons, the concentration profiles in figures 1(*b*), 2 and 4 should have a horizontal tangent for $\rho = 0$, i.e. at the centre of the sphere. Such a behaviour cannot be deduced from our MC data, since this region is vanishingly small for $\rho_0 < 1.5$, while lattice points are discreet and separated by finite distances. Thus, chain configurations take discreet values, unlike what happens for actual polymer chains, and the same may be said for mean distances. Further, the precision of the MC data is least at the centre of the sphere, where the central 'shell' (=sphere, in this case) has the smallest volume and contains the smallest number of lattice points (in some instances a single point). For these reasons, it should be kept in mind that the concentration profile curves in figures 1, 2 and 4 are only approximate in the vicinity of $\rho = 0$.

A finding of the present investigation is that if proper reduction lengths are used for RFWs and SAWs ($0.922N^{0.5}$ and $N^{0.592}$, respectively), the concentration profiles inside the enclosing sphere are almost identical. We emphasize that these almost identical concentration profiles correspond, of course, for given chain lengths, to different radii of the confining sphere. For large ρ-values, the RFW concentrations are slightly larger, but a crossover occurs somewhere below $\rho = \rho_0$, and the inverse phenomenon is then observed. This finding may be of some importance, since most theoretical calculations on confined chains rely on RFW statistics. Finally, the fact that concentration profiles of RFWs and SAWs are, inside a given sphere, different and somehow homothetical should be of importance when discussing partition of macromolecules in free space and inside pores. However, this point cannot be discussed before the entropy problem is developed, and is therefore left to a forthcoming paper.

References

[1] de Gennes P-G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
[2] Casassa E F 1967 *Polym. Lett.* 6 773
[3] Edwards S F and Freed K F 1969 *J. Phys. A: (Gen. Phys.) Ser. 2* 2 145
[4] Collins R and Wragg A 1969 *J. Phys. A: (Gen. Phys.) Ser. 2* 2 151; 1972 *J. Phys. A: Gen. Phys.* 5 1196
[5] DiMarzio E A and Rubin R J 1971 *J. Chem. Phys.* 55 4318
[6] Wall F T, Mandel F and Chin J C 1976 *J. Chem. Phys.* 65 2231
[7] Wall F T, Chin J C and Mandel F 1977 *J. Chem. Phys.* 66 3066
[8] Wall F T, Seitz W A and Chin J C 1977 *J. Chem. Phys.* 67 434

[9] Daoud M and de Gennes P-G 1977 *J. Physique* **38** 85
[10] Guttmann A J and Whittington S G 1978 *J. Phys. A: Math. Gen.* **11** L107
[11] Webman I and Lebowitz J L 1980 *J. Physique* **41** 579
[12] Vilanove R and Rondelez F 1980 *Phys. Rev. Lett.* **45** 1502
[13] Barr R, Brender C and Lax M 1980 *J. Chem. Phys.* **72** 2702
[14] Eisenriegler E, Kremer K and Binder K 1982 *J. Chem. Phys.* **77** 6296
[15] Kremer K and Binder K 1984 *J. Chem. Phys.* **81** 6381
[16] Ishinabe T 1985 *J. Chem. Phys.* **83** 423
[17] Dayantis J and Sturm J 1985 *Polymer* **26** 1631
[18] Baumgärtner A and Muthukumar M 1987 *J. Chem. Phys.* **87** 3082
[19] Cifra P, Bleha T and Romanov A 1987 *Synthetic Polymeric Membranes* ed B Sedlacek (Berlin: Gruyter); 1988 *Polymer* **29** 1664
[20] Kumar S K, Vacatello M and Yoon Do Y 1988 *J. Chem. Phys.* **89** 5206
[21] Dickman R and Hall C K 1988 *J. Chem. Phys.* **89** 3168
[22] Whittington S G and Soteros C E 1991 *Isr. J. Chem.* **31** 127
[23] Wall F T, Hiller L A and Wheeler D J 1954 *J. Chem. Phys.* **22** 1036
Wall F T, Hiller L A and Atchison W F 1955 *J. Chem. Phys.* **23** 913, 2314; 1957 *J. Chem. Phys.* **26** 1742
Wall F T and Erpenbeck J J 1959 *J. Chem. Phys.* **30** 634, 637
[24] Wall F T, Windwer S and Gans J P 1963 *Methods in Computational Physics* vol 1 (New York: Academic)
[25] Rosenbluth M and Rosenbluth A 1955 *J. Chem. Phys.* **23** 356
Suzuki K and Nakata Y 1970 *Bull. Chem. Soc. Japan* **43** 1067
[26] McCrackin F 1967 *J. Chem. Phys.* **47** 1980; 1972 *J. Res. Nat. Bur. Stand. B. Math. Sci.* **76B** 193
[27] Batoulis J and Kremer K 1988 *J. Phys. A: Math. Gen.* **21** 127
[28] Smoluchowski M 1915 *Wien. Ber.* **124** 263; 1916 *Physik. Zeits* **17** 557, 583
[29] Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
[30] Baumgärtner A 1984 *Applications of the Monte Carlo Method in Statistical Physics* ed K Binder (Heidelberg: Springer)
Rapaport D C 1985 *J. Phys. A: Math. Gen.* **18** 113
Madras N and Sokal A D 1988 *J. Stat. Phys.* **50** 109
Dayantis J and Palierne J F 1991 *J. Chem. Phys.* **95** 6088
[31] Zifferer G 1990 *Makromolekulare Chem.* **191** 2717
Dayantis J and Palierne J F 1994 *Phys. Rev.* B **47** 3217
[32] Wu D, Hui K and Chandler D 1992 *J. Chem. Phys.* **96** 835