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Statistics of confined self-avoiding walks: II. Entropy and pressure of confinement

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Abstract. Self-avoiding walks (SAWs) up to 198 steps and random-flight walks (RFWs) up to 598 steps were computer generated. The entropy change upon confinement of the walks, as well as the pressure exercised by corresponding chains obeying Hamiltonian mechanics on the surface of the confining spheres, was derived from the Monte Carlo data for the 'compactness' parameter W of the walks. If appropriate reduced radii $\rho_0 = R/\langle r \rangle$ are introduced, where $\langle r \rangle$ is the mean end-to-end distance, it is found, in accord with theory, that a plot of the entropy change ΔS versus ρ_0^2 for RFWs is linear. The same is also found to be true for SAWs, though in a somewhat more limited ρ_0 range. The quantity PV/KT, where P is the pressure, V the volume of the confining boundary, T the absolute temperature, and K is Boltzmann's constant, is also found to vary linearly with ρ_0^2, for both kinds of walks, in accord with the Edwards-Freed theory. The general conclusion to be drawn from the present paper and also a previous one, is that if proper reduction lengths are introduced for SAWs and RFWs (respectively, $N^{0.592}$ and $0.922\,N^{0.5}$), then the general properties of confined SAWs and RFWs are quite comparable. These properties include chain dimensions, concentration profiles, entropy change upon confinement, and finally pressure.

1. Introduction

In a previous article [1], using Monte Carlo (MC) simulations, the dimensions and concentration profiles of random-flight walks (RFWs) and self-avoiding walks (SAWs) confined inside spheres of varying diameter were reported. In the present article, the entropy and related quantities of such walks are presented.

The problem of the entropy of RFWs confined in various geometries, including spheres, was addressed analytically by Casassa [2]. Sometime later, Edwards and Freed [3], and Collins and Wragg [4], addressed the equivalent problem of RFWs confined inside a cube. Cifra *et al* [5] made MC simulations of SAWs confined inside a cube, and determined the partition function and thus the entropy of such walks. Analytical, exact enumeration, and Monte Carlo studies of confined chains, whether RFW or SAW, are numerous [2-22], however, it seems that the specific problem of the spherical boundary has been for some reason neglected. The motivation or background of many of these studies is in fact the adsorption of polymers on a surface, and therefore the constraint considered in such cases is one or two parallel plane surfaces. On the other hand, the entropy problem inside spheres, is important in gel permeation chromatography, for chain polymerization inside small droplets, and more generally for the thermodynamics of polymer chains inside droplets, as this happens in microemulsions [23]. The present MC study of chains confined in spheres should, however, be primarily viewed as a study

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in its own right of walks confined inside a passive (zero-infinite potential) boundary of spherical shape.

The computational software and methods used in this article are the same as in the previous article [1] and will not be repeated here. In particular, the reader is referred to [1] for the basic features of absorbing (AS) and reflecting (RS) statistics. For convenience, we remind here that the attrition $A(N, R)$ is the probability of failure of an initiated walk. In AS and for SAWs, the attrition $A_{AS}(N, R)$ of an N-step walk inside a sphere of radius R originates in that a given lattice site cannot be visited twice by the walk being generated, and by the fact that the walk cannot cross the surface of the sphere. In reflecting statistics (RS), the attrition $A_{RS}(N, R)$ originates in the fact that the SAW being generated may become trapped inside a nest. A_{RS} is usually a negligible quantity, unless the dimensions of the bounding surface become comparable to or smaller than the mean dimensions of the free (unbounded) N-step walk. In any case, A_{RS} is always considerably smaller than A_{AS}, and therefore, in order to save computational time, RS will generally have to be used.

We also remind the reader of the definition of the 'compactness' parameter W, occurring in RS [1, 24, 25]:

$$W=(SZ_{\max})^{-1}\left\{\sum_{j=1}^{S}\prod_{i=1}^{6}(i)\right\}^{n_i^j}. \tag{1a}$$

Here n_i^j represents in how many cases there were, for chain j in the sample, i possibilities to continue the generation process of the walk; S is the sample size, and $Z_{\max}$ is defined through:

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

$$Z_{\max}=6^N \qquad \text{(RFWs)}. \tag{1c}$$

2. Theoretical relationships

In order to analyse and correlate the Monte Carlo data, a number of theoretical relationships are needed. First, a Monte Carlo estimate of the number $Z(N, R)$ of distinct configurations of the N-step confined walk inside the sphere R is required.

In AS, the solution to this problem is obvious, since, if $A_{AS}(N, R)$ is the attrition, one clearly has for the mean number of configurations per bounded lattice site:

$$Z_p(N, R)=Z_{\max}(N)[1-A_{AS}(N, R)] \tag{2}$$

where $Z_{\max}(N)$ is the number of configurations of the free random-flight walk of N steps, given in (1c). The total number $Z(N, R)$ of distinct N-step configurations inside the sphere of radius R containing k lattice sites is then:

$$Z(N, R)=Z_{\max}(N)[1-A_{AS}(N, R)]k. \tag{3}$$

In RS, $Z(N, R)$ may be estimated through the expectation $E(W)$ of the $W(N, R)$ parameter as follows: let us assume that using RS we start generating N-step walks starting from lattice sites chosen at random inside the sphere R. Let us further assume that in a total sample of S trials, S_a have succeeded and $S-S_a$ have failed (=the walk get trapped inside a nest before being completed). If w^j is the weighing factor of walk

j in the sample, then the MC expectation of W is

$$E_{MC}(W) = S^{-1}\left\{\sum_{j=1}^{S_a} w^j + \sum_{j=S_a+1}^{S} w^j\right\}. \tag{4}$$

Now, the failing walks are not counted in MC statistics, and therefore the second sum in the RHS of equation (4) is zero. Thus

$$E_{MC}(W) = S^{-1}\left(\frac{S_a}{S_a}\right)\left(\sum_{j=1}^{S_a} w^j\right) = (S_a/S)S_a^{-1}\left(\sum_{j=1}^{S_a} w^j\right) = [1 - A_{RS}(N, R)]W_{MC} \tag{5}$$

where W_{MC} is the MC-obtained mean value of the w^js. On the other hand the theoretical expectation of W is

$$E_{th}(W) = \sum_{j=1}^{Z(N,R)} p_j w^j \tag{6}$$

where p_j is the probability of constructing the specific walk j, where j covers all the range of accessible configurations. Now $p_j = p_s p(j/s)$, that is p_j is equal to the product of the probability p_s of starting a walk at the lattice site s, by the conditional probability $p(j/s)$ of obtaining configuration j, if it is known that the starting site s has actually been chosen. Since all starting sites have to be taken with equal probabilities, the first probability is equal to k^{-1}, where k is the number of lattice sites bounded by the sphere. The second probability is

$$p(j/s) = \prod_i (i)^{-n_i^j} \tag{7}$$

where n_i^j is the number of occurrences where there have been i possible directions to continue generating the walk. From equations (1) and (7) it is seen that

$$p(j/s) = (w^j Z_{max})^{-1}. \tag{8}$$

Combining equations (6) and (8) one finds

$$E_{th}(W) = Z/kZ_{max}. \tag{9}$$

Now the theoretical and MC values of the expectation $E(W)$ should be approximately equal quantities. (The deviation due to statistical fluctuations of $E_{MC}(W)$ may be reduced by increasing the MC sample S). One then has, from equations (5) and (9) the following estimate for $Z(N, R)$:

$$Z(N, R) = Z_{max}(N)[1 - A_{RS}(N, R)]W(N, R)k. \tag{10}$$

This is the basic relationship we shall use in the following; it constitutes an elaboration of the general relationships given in [24] and [25]. The mean number of configurations per lattice site is equal to

$$Z_p(N, R) = Z_{max}(N)[1 - A_{RS}(N, R)]W(N, R). \tag{11}$$

From equation (10) the entropy of an N-step chain (a chain being a walk whose steps are interconnected) inside the sphere R, provided it obeys Hamiltonian mechanics, is given by

$$S(N, R)/K = \ln Z(N, R) \tag{12a}$$

where K is Boltzmann's constant.

Similarly, the mean entropy per lattice site inside the boundary is given by

$$S_p(N, R)/K = \ln Z_p(N, R). \tag{12b}$$

The above relationships (10) to (12) are general. They are valid for SAWs and for RFWs as well, provided that the proper values for the attrition A and the compactness parameter W are used. They are also valid whether the walk is free or confined, and for any configurations of bounding surface.

We can now consider the number of configurations of the free (unbounded) walk per lattice site:

$$Z_p(N, \infty) = Z_{max}[1 - A_{RS}(N, \infty)]W(N, \infty). \tag{13}$$

For an unbounded RFW the attrition is zero and the compactness parameter equal to one, so that in this case $Z_p(N, \infty) = Z_{max}$, as expected. This is no longer true for an unbounded SAW, though in this case for most lattices the attrition A_{RS} is quite small and thus negligible.

From (11) and (13) one has for the entropy change per lattice site upon confinement of a free walk:

$$\begin{aligned}\Delta S/K &= [S_p(N, R) - S_p(N, \infty)]/K = \ln[Z_p(N, R)/Z_p(N, \infty)] \\ &= \ln\{[1 - A(N, R)W(N, R)/[1 - A(N, \infty)]W(N, \infty)\}\end{aligned} \tag{14a}$$

where for simplicity in the attrition the subscript RS has been dropped. If, as generally happens when the radius of the sphere is large with respect to the chain dimensions, both $A(N, \infty)$ and $A(N, R)$ are small, one can simply write:

$$\Delta S/K = \ln[W(N, R)]/(W(N, \infty)]. \tag{14b}$$

Relations (14) refer to the mean entropy change per lattice site, since the actual entropy of chains originating in specific bounded lattice sites depends on the specific site considered.

It follows from classical statistical mechanics that

$$\begin{aligned}P &= -(\partial F/\partial V)_T = T(\partial S/\partial V)_T = KT\{(\partial/\partial V) \ln[Z(N, R)] \\ &= [KT/4\pi R^2](\partial/\partial R) \ln[Z(N, R)].\end{aligned} \tag{15}$$

Here P is the pressure exercised by the chain upon the spherical boundary, F is the free energy, V the volume, T the absolute temperature, and $Z(N, R)$ is given by equation (10).

Beyond the comparison of the properties of N-step confined chains with or without excluded volume, it may be of some interest to compare the properties of an N-step chain with a gas of N independent molecules, with or without excluded volume (the latter case corresponding to the perfect gas). Since we used a discrete lattice to generate our N-step chains, the comparison should proceed using the corresponding relationships for a gas, the molecules of which are constrained to occupy discrete lattice sites. With this assumption, if there are k lattice sites within the sphere of radius R, the entropy of N independent molecules experiencing excluded volume is given by

$$S/K = \ln[k!/(k - N)!N!] = -\{(k - N) \ln[(k - N)/k] + N \ln[N/k]\} \tag{16}$$

where, to obtain equation (16), indiscernibility of the molecules has been assumed, and Stirling's approximation for the factorials used. The pressure follows by introducing

(16) into (15):

$$P = -KT \ln[1 - N/k]. \tag{17}$$

In the absence of excluded volume, the entropy is given by

$$S/K = \ln[k^N/N!] \tag{18}$$

and correspondingly the pressure is

$$P = KTN/k. \tag{19}$$

If the number of lattice sites is nearly proportional to the volume V of the sphere, the perfect gas law $PV = NKT$ follows from equation (19). However, for the relatively small sphere volumes occurring in our calculations, the proportionality is only approximate, and therefore it is preferable to calculate the entropy and pressure of N confined independent gas molecules using equations (16) to (19).

3. Monte Carlo results

From equations (3) and (10) one obtains:

$$W = (1 - A_{AS})/(1 - A_{RS}) \tag{20}$$

a relationship relating the compactness parameter to the attritions in absorbing and reflecting statistics. This relationship has been checked for various values of ρ_0, where ρ_0 is the reduced radius of the confining sphere, that is the radius R over the mean end-to-end distance $\langle r \rangle$ of the free chain.

In tables 1 and 2 the W parameter is tabulated as a function of ρ_0, for SAWs and RFWs, respectively, and for step lengths ranging from 18 to 58 steps. These tables also display the corresponding square standard deviations $\sigma^2_W = \langle w^2 \rangle - \langle w \rangle^2$.

From tables 1 and 2 for W, the analogous tables for the entropy change $\Delta S/K$ upon confinement of the chain, and the pressure P exercised by the chain on the bounding surface, as a function of ρ_0 (rather, ρ_0^{-2}, see below) are easily established. To this end, equations (10), (12*a*) and (15) have to be used. As a consequence of this, the information provided by the latter tables is already contained in tables 1 and 2, and therefore such tables would be somewhat redundant. For this reason, only the corresponding diagrams will be given, with the exception of PV/KT, which for convenience is tabulated in table 3. In table 4, the parameters of the linear regressions in the linear part of the plots of $\Delta S_p = f(\rho_0^{-2})$ are tabulated (see the discussion).

In figures 1 and 2, the entropy variation per lattice site upon confinement of a SAW or a RFW is given, as a function of ρ_0^{-2}. ρ_0^{-2} has been chosen as variable in these figures instead of ρ_0, because it is known from theory [2], that for RFWs, when the radius of the confining sphere approaches the dimensions of the free chain, the entropy change ΔS is linear in this variable. Figure 1 is concerned with small ρ_0^{-2} values (large R radii), while figure 2 is concerned with large ρ_0^{-2} values (small R radii). Figure 3 displays the overall entropy variation, the quantity relevant for calculation of the pressure through equation (15). Finally, figure 4 shows the pressure felt by the sphere boundary when an N-step SAW or RFW chain, obeying Hamiltonian mechanics, is confined inside the sphere. For comparison, the pressures corresponding to N independent (gas-like) molecules, with or without excluded volume, is also given.

Table 1. Compactness parameter W for SAWs, as a function of the number of steps in the confined walk and the reduced radius of the confining sphere. Below the W values, the square standard deviations σ^2_W are also listed. All sample sizes in this table and everywhere else: 10^5 chains.

N	18	28	38	48	58
$\langle r \rangle$	5.52	7.18	8.63	9.89	11.06
ρ_0					
∞	4.88×10^{-1}	2.74×10^{-1}	1.49×10^{-1}	7.98×10^{-2}	4.33×10^{-2}
	6.69×10^{-2}	4.68×10^{-2}	2.45×10^{-2}	1.10×10^{-2}	4.76×10^{-3}
4	3.57×10^{-1}	1.98×10^{-1}	1.08×10^{-1}	5.78×10^{-2}	3.07×10^{-2}
	8.80×10^{-2}	4.57×10^{-2}	2.09×10^{-2}	8.80×10^{-2}	3.51×10^{-3}
3	3.18×10^{-1}	1.74×10^{-1}	9.42×10^{-2}	5.07×10^{-2}	2.74×10^{-2}
	8.70×10^{-2}	4.31×10^{-2}	1.92×10^{-2}	7.92×10^{-3}	3.29×10^{-3}
2	2.43×10^{-1}	1.33×10^{-1}	7.18×10^{-2}	4.64×10^{-2}	2.04×10^{-2}
	7.69×10^{-2}	3.58×10^{-2}	1.52×10^{-2}	6.18×10^{-3}	2.37×10^{-3}
1.5	1.78×10^{-1}	9.80×10^{-2}	5.27×10^{-2}	2.76×10^{-2}	1.48×10^{-2}
	6.11×10^{-2}	2.72×10^{-2}	1.11×10^{-2}	4.31×10^{-3}	1.71×10^{-3}
1.2	1.25×10^{-1}	6.76×10^{-2}	3.59×10^{-2}	1.92×10^{-2}	1.01×10^{-2}
	3.52×10^{-2}	1.54×10^{-2}	6.09×10^{-3}	2.41×10^{-3}	9.14×10^{-4}
1.0	8.75×10^{-2}	4.38×10^{-2}	2.30×10^{-2}	1.19×10^{-2}	6.33×10^{-3}
	2.73×10^{-2}	1.08×10^{-2}	4.25×10^{-3}	1.58×10^{-3}	6.26×10^{-4}
0.8	3.89×10^{-2}	1.78×10^{-2}	9.92×10^{-3}	5.40×10^{-3}	2.75×10^{-3}
	8.83×10^{-3}	3.22×10^{-3}	1.36×10^{-3}	5.43×10^{-4}	1.98×10^{-4}
0.6	5.08×10^{-3}	3.15×10^{-3}	1.58×10^{-3}	8.75×10^{-4}	4.17×10^{-4}
	3.46×10^{-4}	2.23×10^{-4}	8.50×10^{-5}	3.65×10^{-5}	1.49×10^{-5}
0.5	1.06×10^{-3}	4.09×10^{-4}	2.54×10^{-4}	1.23×10^{-4}	7.31×10^{-5}
	7.65×10^{-6}	3.84×10^{-6}	3.26×10^{-6}	9.44×10^{-7}	5.65×10^{-7}

Table 2. Same parameters as in table 1 for RI-Ws.

N	18	28	38	48	58
$\langle r \rangle$	3.92	4.88	5.68	6.39	7.02
ρ_0					
4	7.05×10^{-1}	6.96×10^{-1}	6.94×10^{-1}	6.91×10^{-1}	6.87×10^{-1}
	1.53×10^{-1}	1.66×10^{-1}	1.73×10^{-1}	1.78×10^{-1}	1.82×10^{-1}
3	6.19×10^{-1}	6.10×10^{-1}	6.03×10^{-1}	5.98×10^{-1}	5.94×10^{-1}
	1.69×10^{-1}	1.83×10^{-1}	1.91×10^{-1}	1.97×10^{-1}	2.01×10^{-1}
2	4.57×10^{-1}	4.48×10^{-1}	4.42×10^{-1}	4.39×10^{-1}	4.34×10^{-1}
	1.65×10^{-1}	1.80×10^{-1}	1.88×10^{-1}	1.94×10^{-1}	1.97×10^{-1}
1.5	3.25×10^{-1}	3.10×10^{-1}	3.06×10^{-1}	3.03×10^{-1}	3.02×10^{-1}
	1.32×10^{-1}	1.44×10^{-1}	1.52×10^{-1}	1.57×10^{-1}	1.61×10^{-1}
1.2	2.33×10^{-1}	2.07×10^{-1}	2.07×10^{-1}	1.93×10^{-1}	1.94×10^{-1}
	9.56×10^{-2}	9.76×10^{-2}	1.06×10^{-1}	1.05×10^{-1}	1.10×10^{-1}
1.0	1.43×10^{-1}	1.24×10^{-1}	1.19×10^{-1}	1.09×10^{-1}	1.13×10^{-1}
	5.15×10^{-2}	5.47×10^{-2}	5.95×10^{-2}	5.81×10^{-2}	6.19×10^{-2}
0.8	5.69×10^{-2}	5.70×10^{-2}	4.60×10^{-2}	4.99×10^{-2}	4.60×10^{-2}
	1.20×10^{-2}	1.87×10^{-2}	1.86×10^{-2}	2.22×10^{-2}	2.19×10^{-2}
0.6	8.51×10^{-3}	6.10×10^{-3}	8.13×10^{-3}	9.11×10^{-3}	5.66×10^{-3}
	7.99×10^{-4}	6.09×10^{-4}	1.60×10^{-3}	2.01×10^{-3}	1.32×10^{-3}
0.5	1.79×10^{-3}	6.85×10^{-4}	1.09×10^{-3}	1.21×10^{-3}	9.63×10^{-4}
	9.23×10^{-6}	2.01×10^{-5}	5.63×10^{-5}	1.36×10^{-4}	1.24×10^{-4}

Table 3. PV/KT for self-avoiding walks (SAWs), random-flight walks (RFWs), independent small molecules with excluded volume (IMEV), and independent small molecules without excluded volume (IMNEV), as a function of the number of steps in the confined walk and the reduced radius of the confining sphere.

	SAWs			RFWs		
ρ_0	18	38	58	18	38	58
4.0	1.07	1.10	1.10	1.10	1.13	1.11
3.0	1.09	1.14	1.14	1.15	1.18	1.15
2.0	1.15	1.27	1.17	1.27	1.34	1.30
1.5	1.34	1.44	1.47	1.46	1.50	1.53
1.2	1.65	1.72	1.72	1.84	1.79	1.84
1.0	2.17	2.03	2.06	2.08	1.99	2.14
0.8	2.78	2.54	2.65	2.57	2.56	2.81
0.6	3.43	3.76	3.67	3.90	4.01	3.74
0.5	4.76	5.15	5.05	3.79	4.93	4.71
	IMEV			IMNEV		
4.0	19.01	39.01	59.01	19.00	39.00	59.00
3.0	19.01	39.01	59.01	19.00	39.00	59.00
2.0	19.03	39.04	59.05	19.00	39.00	59.00
1.5	19.08	39.08	59.10	19.00	39.00	59.00
1.2	19.15	39.16	59.18	19.00	39.00	59.00
1.0	19.25	39.29	59.29	19.00	39.00	59.00
0.8	19.51	39.57	59.61	19.00	39.00	59.00
0.6	20.35	40.36	60.45	19.00	39.00	59.00
0.5	21.65	41.43	61.49	19.00	39.00	59.00

Table 4. Parameters of linear regression in the range $0.6 \leqslant \rho_0 \leqslant 2.0$ for the entropy change ΔS_p due to confinement, versus ρ_0^{-2}, where ρ_0 is the reduced radius of the confining sphere, for SAWs and RFWs. a is the slope in the linear regression and b the intercept with the $-\Delta S_p/K$ axis. The correlation coefficient (cc) is listed in the final column.

N	a	b	cc
RFWs			
18	1.58	0.40	1.000
58	1.71	0.44	1.000
198	1.80	0.47	1.000
398	1.85	0.46	1.000
598	1.84	0.48	1.000
SAWs			
18	1.52	0.28	0.998
58	1.53	0.38	1.000
198	1.78	0.32	0.998
198bis	1.80	0.32	0.996

4. Discussion

Figures 1 and 2 show that for equal ρ_0 values, where ρ_0 is the reduced radius of the confining sphere, the entropy variation ΔS_p as a function of ρ_0^{-2} is only slightly different for SAWs as compared to RFWs. For small ρ_0^{-2} values (large confining spheres),

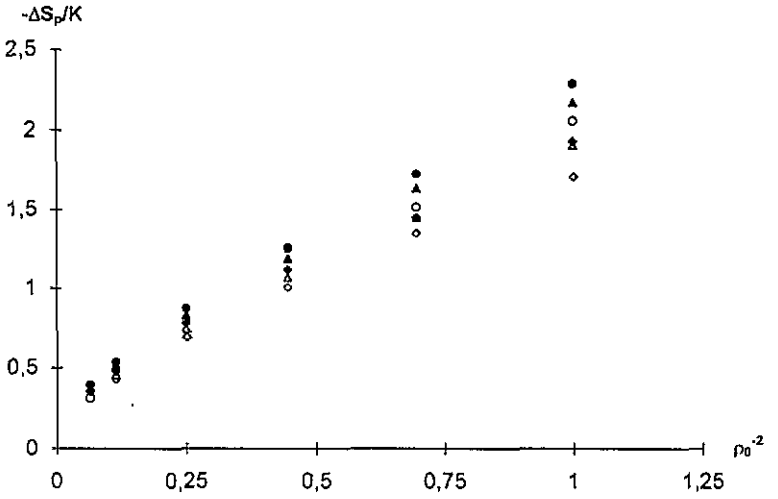

Figure 1. Entropy variation per lattice site upon confinement $-\Delta S_p$, divided by Boltzmann's constant K, versus ρ_0^{-2}, where $\rho_0 = R/\langle r \rangle$ is the reduced radius of the confining sphere, $\langle r \rangle$ being the mean end-to-end distance of the free (non-confined) walk. SAWs: ◇, 18 steps, △, 58 steps, ○, 198 steps; RFWs: ◆, 18 steps, ▲, 58 steps, ●, 198 steps. The figure refers to small values of ρ_0^{-2} (large radii of the confining sphere).

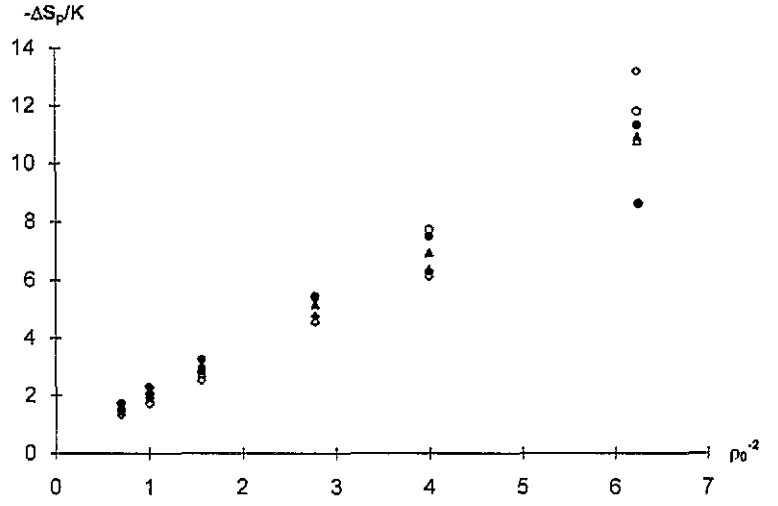

Figure 2. Parameters and notation as in figure 1, but for large values of ρ_0^{-2} (small radii of the confining sphere).

$-\Delta S_{pSAW} < -\Delta S_{pRFW}$; the inverse phenomenon is observed for large ρ_0^{-2} values (small confining spheres), and the latter phenomenon is easily interpreted as being due to the excluded volume of SAWs. However, it should constantly be kept in mind that the reduction lengths $\langle r \rangle$ are different for RFWs and SAWs, as a function of N: these lengths are $0.922\,N^{0.5}$ and $N^{0.592}$, respectively. Thus, for $N = 58$ steps, one has for the radii of the confining spheres at $\rho_0 = 1$, 7.02 and 11.06, respectively [1]. The relative difference in radii increases with N.

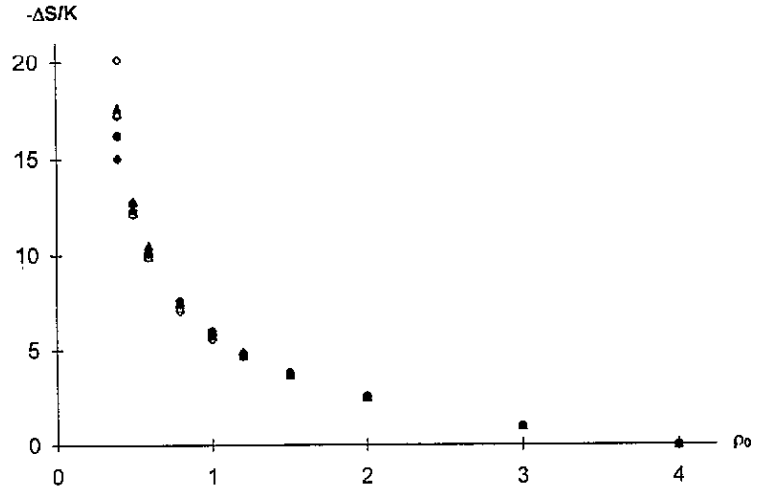

Figure 3. Total entropy variation upon confinement of a walk $-\Delta S$ (not to be confused with the entropy variation per lattice site), divided by Boltzmann's constant K, versus ρ_0, where ρ_0 is the reduced radius of the confining sphere. The reduced radius $\rho_0 = 4$ is arbitrarily taken as the origin. SAWs: ◇, 18 steps, ○, 38 steps, △, 58 steps; RFWs: ◆, 18 steps, ●, 38 steps, ▲, 58 steps.

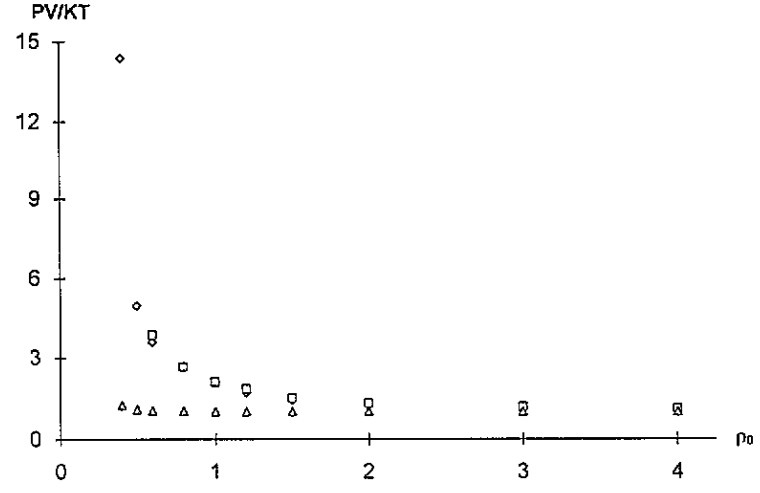

Figure 4. PV/KT, where P is the pressure exercised by the confined chain on the spherical boundary, V the volume of the confining sphere, K Boltzmann's constant and T the absolute temperature, versus ρ_0, where ρ_0 is the reduced radius of the confining sphere. Scaling is obeyed, that is PV/KT does not depend on the number N of steps of the chain, but only on the reduced radius ρ_0 of the confining sphere. ◇, self-avoiding walks (SAWs); □, random-flight walks (RFWs); △, independent small molecules with excluded volume (IMFV). For independent small molecules without excluded volume, PV/KT is equal to one.

The downwards curvature of the plot in figure 1 as ρ_0^{-2} becomes small, is due to the fact that then higher contributions to the Casassa equation (see below), which have been neglected in our analysis, become important. The same downwards curvature is also displayed by SAWs. The linear region in the plots in figure 2 as ρ_0^{-2} is increased is

significantly more extended for RFWs. The dispersion and inversion of points for $\rho_0^{-2} > 4$ is an artefact due to the smallness of the confining spheres, where, due to the small number of lattice sites inside the boundary, the entropy leaps by relatively large and unpredictable amounts as the radius of the confining sphere is varied. The phenomenon of course exists also for large confining spheres, but then the leaps are comparatively small and overshadowed by the large number of bounded lattice sites, and a continuous variation of the entropy is then observed.

Casassa [2] gave a relationship for the partition Q of Gaussian chains inside pores of spherical shape and the bulk solution, which when ρ_0 is less than 2, is approximated by

$$Q_{\text{sphere}} = (6/\pi^2) \exp\{-\pi^2[\langle r^2\rangle/\langle r\rangle^2]/6\rho_0^2\}. \tag{21}$$

Now

$$K \ln Q = \Delta S_p \tag{22}$$

the entropy change when the chain is in bulk solution (free chain), and when it is constrained to lie inside a spherical pore, the chain being started in both cases at specific lattice sites.

From equations (21) and (22) it follows that, for RFWs

$$(\Delta S/K)_{\text{RFW}} = \{\ln(6/\pi^2) - (\pi^2/6)[\langle r^2\rangle/\langle r\rangle^2]\rho_0^{-2}\} \tag{23}$$

that is

$$(\Delta S/K)_{\text{RFW}} = -0.498 - 1.938\rho_0^{-2} \tag{24}$$

where, in (24), the ratio $\langle r^2\rangle/\langle r\rangle^2$ for RFWs has been replaced by its limiting value, 1.178, as N tends to infinity [1]. Now from table 4 it is seen that the limiting MC slope of $(-\Delta S_p/K)_{\text{RFW}}$ versus ρ_0^{-2} appears to be only 1.85 ± 0.02. Explanation of this difference in slope (1.85 instead of 1.94) may be as follows: due to the discrete nature of the cubic lattice on which our walks are embedded, the Casassa equation does not strictly apply to our MC simulations. The Casassa equation has been derived by analogy with the theory of heat. The diffusion equation has been used for the purpose, assuming that the spherical boundary is held to zero temperature. Now when one uses differential equations, one necessarily introduces continuity, whereas our lattice contains discrete lattice sites. In our case, there is a superficial spherical shell of width less than, but of the order of magnitude of the step length, where in the mean the walks are forbidden and therefore cannot reach the boundary. In other words, the 'effective' reduced radius of the confining sphere is not exactly ρ_0, but somewhat less. Of course, the effect of this outer shell would become negligible if very large chains (say $N = 10^6$), could have been contemplated in MC simulations, but this is not the case.

In the range of ρ_0 ($0.6 \leqslant \rho_0 \leqslant 2$) from which the data in table 4 have been derived, the width of the forbidden superficial shell may tentatively be estimated through the relationship

$$1.85\rho_0'^{-2} = 1.94\rho_0^{-2}. \tag{25}$$

Here $\rho_0'^{-2}$ is the effective radius, which will correct for the discrepancies in the slope. For $N = 598$, our largest RFW, $\langle r\rangle = 22.54$, so that the radius of the confining sphere for $\rho_0 = 1$ is 22.54, and the width of the forbidden superficial shell would then be

$$\Delta R = \langle r\rangle \Delta\rho_0 = 22.54 \times 0.0235 = 0.53 \tag{26}$$

that is about half the step length. This is a quite plausible value. The above argument is tentative, not rigorous, and does not apply to large ρ_0 values (for which, however, the simplified Casassa equation (21) does not apply, and in which large ρ_0 values have not been used to establish the data in table 4). If we admit the argument, which in any case cannot be discarded, then, notwithstanding the nearly 5% difference between the theoretical and MC slopes, one can assume that the agreement of our MC data with the Casassa theoretical prediction is good. Finally, as deduced from table 4, there is satisfactory agreement regarding the constant term, which yields the prefactor $6/\pi^2$ in equation (21).

On the other hand, the results for SAWs show (see figures 1 and 2 and table 4) that there is a range of ρ_0, somewhat more restricted than for RFWs, where ΔS scales as ρ_0^{-2}, with a slope which differs but little from that of RFWs.

One might have wished to be able to compare these results with those of scaling theories for confined SAWs. Unfortunately, all papers of which we are aware are concerned with SAWs confined inside slits or tubes. That means that whatever the dimensions of the confining slits or tubes, at least one dimension remains infinite, which is not the case if the confining geometry is a sphere. From this it follows that direct transposition to a spherical boundary of the scaling arguments given, e.g. by Daoud and de Gennes [10], does not appear to be feasible. The one thing we can say with certainty, is that in a ΔS versus ρ_0^{-2} diagram, both SAWs and RFWs display nearly the same slope. A $\ln[-\Delta S]$ versus $\ln \rho_0$ plot, not reproduced here, shows that SAWs scale with respect to ρ_0, with a power which is equal or perhaps somewhat larger than that of RFWs.

Regarding now PV/KT, the number equivalent m of independent small molecules which will produce the same pressure as one SAW or RFW chain is given in table 5. The PV/KT data have been obtained by expanding $\Delta S/K$ as a series in $\rho_0^{0.5-i}$ (i up to seven) and deriving the series with respect to ρ_0 to obtain the pressure through equation (15). Though this expansion does not contain the leading term ρ_0^{-2}, it was empirically found to yield the best fit, surely through compensation effects. It is seen from table 3 that scaling is obeyed, and that PV/KT is about the same for SAWs and RFWs for equal values of ρ_0. m is about 2 for ρ_0 equal to 1, and about 5 for ρ_0 equal to 0.5. It is expected that as ρ_0 decreases below this value, $(PV/KT)_{\mathrm{SAW}}$ would increase much more steeply than $(PV/KT)_{\mathrm{RFW}}$, because of the excluded volume of SAWs. A MC analysis of this expectation is however difficult, because for small radii the small number of bounded lattice sites yields data which vary erratically and cannot be used.

The results in table 3 will now be compared with the Edwards–Freed (EF) theory for the pressure exercised by a random flight chain on the walls of a cubic box [3]. If the step length is ascribed the value 1, as is the case in the present work, the EF theory leads to an equation which may be written in present notation as

$$(PV/KT)_{\mathrm{RFW}} = (\pi^2/3)[N/V^{2/3}] = (\pi^2/3)[\langle r^2\rangle/V^{2/3}] \tag{27}$$

where V is the volume of the cubic box. If we assume that the above relationship remains valid for a spherical boundary and replace V by $(4/3)\pi R^3$, making also the conversion to the reduced variable $\rho_0 = R/\langle r\rangle$ used here, one obtains

$$(PV/KT)_{\mathrm{RFW}} = 1.226[\langle r^2\rangle/\langle r\rangle^2]\,\rho_0^{-2} = 1.49\rho_0^{-2} \tag{28}$$

where $\langle r^2\rangle/\langle r\rangle^2$ has been replaced by its limiting value 1.178. From table 3, considering the mean values of $(PV/KT)_{\mathrm{RFW}}$ for 18, 38 and 58 steps, in the range $0.6 \leqslant \rho_0 \leqslant 4.0$,

Table 5. Number equivalent m of small independent molecules, which will produce the same pressure as a single RFW chain, as a function of ρ_0^{-2}, where ρ_0 is the reduced radius of the confining sphere

ρ_0	4.0	3.0	2.0	1.5	1.2	1.0	0.8	0.6
ρ_0^{-2}	0.0625	0.1111	0.25	0.4444	0.6944	1.0	1.5625	2.7777
m	1.11	1.16	1.30	1.50	1.82	2.07	2.65	3.88

one finds the number equivalent m of small molecules given in table 5. The data in this table yield a straight line of slope nearly 1 and correlation coefficient 1.000. Thus, it appears that in accord with the EF theory, m varies linearly with ρ_0^{-2}, but the MC slope is only 1, instead of 1.5. We do not know if this discrepancy originates in the different geometric form of the bounding surface, or in some other reason.

Finally, regarding gel permeation chromatography, the findings in the present paper do not lead to a unique conclusion. In a theta solvent, polymer chains recover the dimensions of RFW chains of the same number of steps, and can most aptly be described as pseudo-RFWs. There is then no reason not to assume that the Casassa theory is an adequate description of actual phenomena. In an athermal solvent, on the other hand, the behaviour of polymer chains will approximately approach that of the SAWs here considered†. In this case, the reduced diameter of the pores is not that applying to RFWs, and the Casassa theory will overestimate the ease with which polymer chains enter pores, and thus the partition coefficient Q. However, the theory can in this case be corrected, to a fair or good degree of approximation, by a simple renormalization of the pore diameters. The error involved when so doing may be estimated, according to the parameter involved, from the tables and figures of this paper and those of [1]. Intermediate situations between good and theta solvents may be treated accordingly.

5. Conclusions

Provided that proper reduction lengths are used for N-step confined SAWs and RFWs ($N^{0.592}$ and $0.922N^{0.5}$, respectively), then for equal values of the reduced radii of the confining spheres, both these walks exhibit very comparable behaviours for all the quantities investigated in the present and in the previous paper [1]. These quantities include chain dimensions, concentration profiles, entropy change upon confinement, and pressure exercised by the confined walk (=chain) on the confining boundary. On the other hand, if identical values for the dimensions of the confining geometries are considered (which means that the reduced dimensions are now different), then the behaviours of confined SAWs and RFWs are no longer comparable.

Thus, it appears that one can derive, to a fair and perhaps sometimes good degree of approximation, the properties of confined SAWs inside spheres, from the analytically more tractable theory of confined RFWs, through a simple renormalization of lengths. This simple result will not in general apply to other confining geometries, in particular when at least one dimension remains infinite.

† Only approximately approach, because the energy of interaction between polymer segments lying far apart along the chain is in fact a free energy, and therefore, even in an athermal solvent, there will be a non-zero free energy of interaction.

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