

# Monte-Carlo calculations on statistical chains enclosed inside a sphere

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(Received 5 July 1984)

Statistical chains have been generated inside a sphere of variable radius  $R$ . The mean square root end-to-end distance, the radius of gyration, and the entropy of the chains have been determined as a function of  $R$  for absorbing boundary (AB) and reflecting boundary (RB) statistics to be defined below in this paper. It is found that the entropy change  $\Delta S$  from the unbounded (free) chain varies as  $R^{-2}$  for AB statistics and as  $R^{-1}$  for RB statistics.

(Keywords: chain statistics; confined chains; entropy; voids; adsorption; Monte-Carlo calculations)

## INTRODUCTION

The effect of voids or boundaries on chain statistics has long been considered<sup>1-3</sup>, particularly in connection with problems of practical interest such as gel permeation chromatography<sup>1-4</sup> (g.p.c.). It has usually been assumed that the entropy of confined chains can be theoretically derived through use of the diffusion equation<sup>1-2</sup>. This implies that the boundary acts on the confined chain in an 'absorbing' fashion; this will be defined in detail in this paper. For simple molecules (gas molecules) it is easy to show that boundaries cannot act in an absorbing fashion; instead, they are acting in a 'reflecting' way, again to be defined below. In the case of macromolecules, here idealized by statistical chains, the situation is more complex; it seems probable, however, that when the dimensions of the voids are small with respect to those of the chain, the boundary does not act on the chain in an absorbing way.

The purpose of the present work is to point out some difficulties which arise when it is taken for granted, as has happened until now, that a boundary acts on a confined chain in an absorbing fashion, irrespective of the relative dimensions of the boundary and the chain in its unperturbed (free) state. Use of the diffusion equation to calculate the entropy of a confined chain is justified only in so far as the boundary is absorbing and the 'absorbing boundary statistics', to be defined below, are obeyed.

## GENERAL CONSIDERATIONS

We consider firstly a statistical chain generated stepwise using a computer inside a specified three-dimensional network. The chain is assumed to be statistical, i.e. different segments in the chain may overlap and there is no excluded volume. If there are no obstacles, such as a boundary interfering with the generation process (free chain), then the number of configurations available to a chain of  $N$ -steps is  $Z_0 = z^N$ , where  $z$  is the coordination number in the process, which is a function of the particular generation process being considered.

If we consider next that the first step of the chain should be located inside some closed boundary and that no step is

allowed to cross that boundary during the generation process of the chain, then clearly the presence of a boundary reduces the number of configurations available to the chain. However, a second possible effect of the boundary may be to affect the statistical weight of the permitted configurations (those lying inside the boundary). In other words, while in the absence of a boundary all configurations are given the same statistical weight, in the presence of a boundary the permitted configurations (those not crossing the boundary) may or may not be given the same statistical weight. If all permitted configurations are given the same statistical weight, the boundary is termed 'absorbing'; otherwise, it is termed 'reflecting'. It is now necessary to deal in some detail with the statistics of chain generation originating from the above two types of boundaries. At the same time this discussion will make clear the reason for the terms 'absorbing' and 'reflecting'.

### *Absorbing boundaries*

If the boundary is absorbing, when a statistical chain is generated starting from a point inside a closed boundary\*, there are two possibilities: either, after  $N$  steps, the generated configuration never crosses the boundary, in which case it is accepted as an element of the Monte-Carlo calculations; or, it does cross the boundary at least once, in which case it is discarded. The effect of the boundary can thus be considered 'absorbing' the configurations crossing it. This 'absorption' is of course quite distinct from the usual adsorption found in the physical chemistry of surfaces or interfaces. The latter phenomenon is an energetic one (or, rather, a free energy one), whilst here, from the energetic standpoint, boundaries are purely neutral, and only entropic phenomena are acting. This point is essential, and therefore again emphasized later<sup>5</sup>. By virtue of the absorbing boundary sampling procedure, all allowed configurations are given the same statistical weight. The effect of the boundary is only to eliminate the configurations crossing it, without

\* In what follows the boundary will always be a sphere of radius  $R$ , but the results thus obtained are of general interest

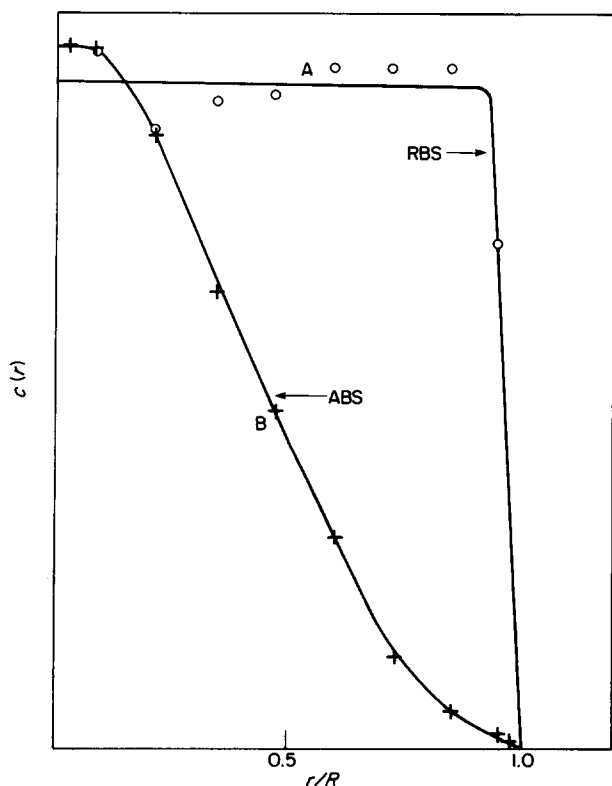
changing the probability of occurrence of the remaining ones. The Monte-Carlo calculations discussed in the Results and Discussion section show that the concentration profile of segments from the centre of the sphere for  $R \approx N^{1/2}$  is a monotonously decreasing function with the maximum value at the centre of the sphere and a value close to zero near the surface of the sphere (Figure 1). For  $R > 3r_g^0$ , there is a plateau region near the centre and then the concentration decreases at a distance of the order  $2r_g^0$  from the boundary (Figure 2).

Absorbing boundaries are consistent with the solution of the diffusion equation; solution of this equation with the appropriate boundary conditions<sup>1-2</sup> leads to a variation  $\Delta S$  of the configurational entropy of the chain with respect to the free chain which is proportional to the inverse square of the characteristic length of the enclosing boundary, at least when this length does not considerably exceed the characteristic length  $r_g^0 \sim N^{1/2}$  of the chain.

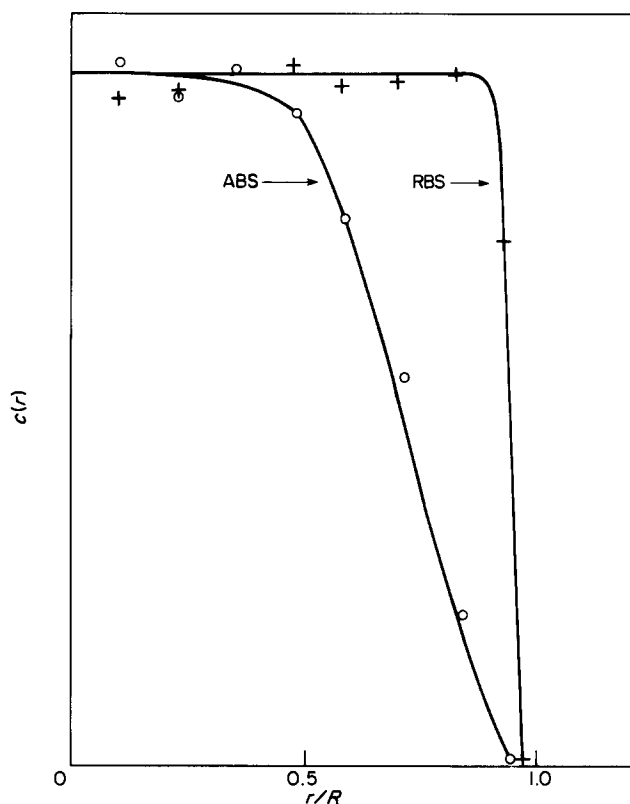
### Reflecting boundaries

The chain generation process is initiated as previously described. However, when a step crosses the boundary, the part of the chain already generated is not discarded; instead, the computer is ordered to go one step back (or more if necessary), and a new direction, which does not cross the boundary, is then followed. The process is repeated each time a step crosses the boundary until completion of the  $N$  steps of the chain. Thus the reflecting boundary somehow 'corrects' configurations which are trespassing, instead of discarding them.

Reflecting boundary statistics (RBS) do not preserve equal probabilities for the allowed configurations, i.e. those inside the boundary. (Of course, the nature of the

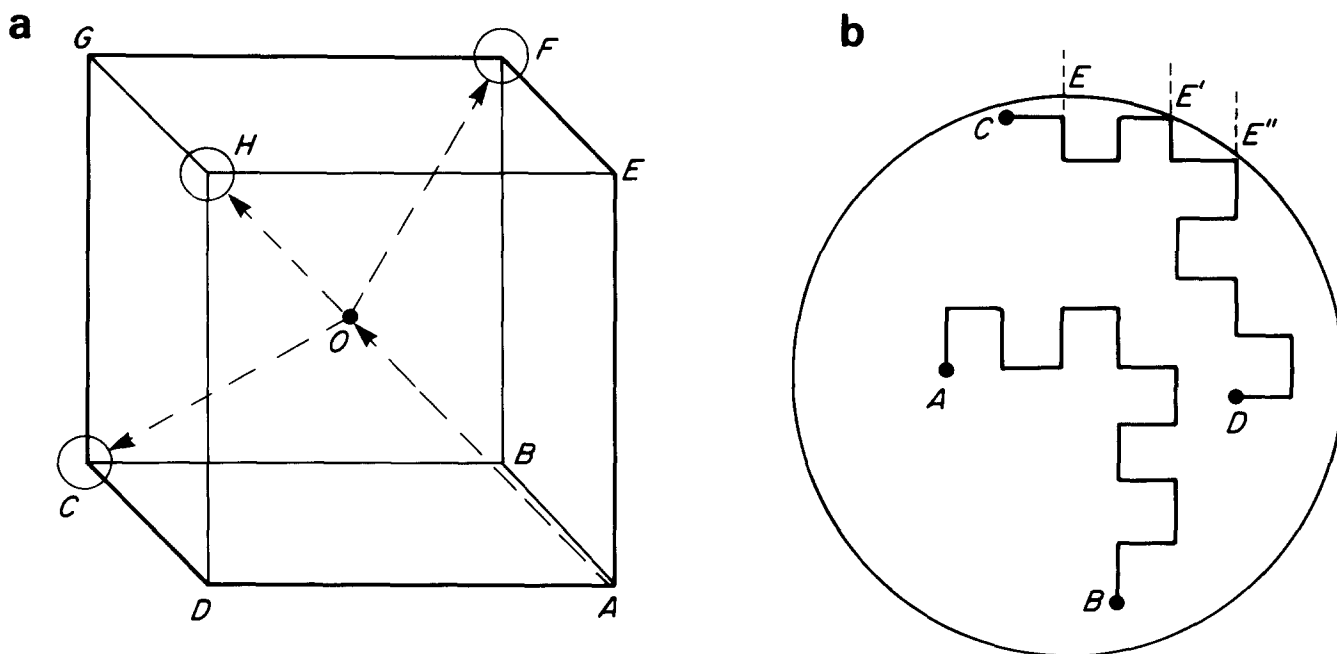


**Figure 1** Concentration profile for absorbing and reflecting boundary statistics, when  $R = 1.1r_g^0$ . The Monte-Carlo sampling comprises 1000 configurations for RB statistics and 50 configurations for AB statistics, the latter case involving 10 days of continuous use of the computer. Ordinate scale is not the same for the two statistics



**Figure 2** Concentration profile for absorbing and reflecting boundary statistics, when  $R$ , the radius of the enclosing sphere is  $5r_g^0$ , where  $r_g^0$  is the radius of gyration of the free (unbounded) chain of index  $N = 1000$ . The Monte-Carlo sampling comprises 10 000 configurations for each kind of statistics. Ordinate scale is not the same for the two statistics

boundary does not change their number, it can only change their respective statistical weights.) To see this, let us consider Figure 3b where two configurations of  $N$  steps are shown, one with all its segments far apart from the boundary (AB), while the other displays several segments in close vicinity to it (CD). For a chain starting at A there is only one way of completing the  $N$  steps up to B; so, the statistical weight is one. However, for the chain starting at C, there is more than one way to reach point D. Firstly, there is the 'normal' way, without crossing the boundary at one or several of the points  $E, E', E'' \dots$ . Then, there are the routes that first cross the boundary at one of the points  $E, E', E'' \dots$  or a combination of these points, and are then 'corrected' in order to follow a permitted direction. Normally, in the absence of the boundary, steps reaching points  $E, E', E'' \dots$  would generate configurations different from the configuration CD shown in Figure 3b. Therefore, one can see that there are several ways of generating the chain CD, and thus the statistical weight to be assigned to these configurations is greater than 1: configurations close to the boundary are favoured with respect to the others. Monte-Carlo statistics using a reflecting boundary (see Figures 1 and 2) show that the concentration of segments from the centre of the confining sphere is constant up until the immediate vicinity of the boundary at a distance of a few steps. The concentration profile does not depend on the ratio of characteristic lengths  $R$  and  $r_g^0 \sim N^{1/2}$ . This behaviour is quite different from that of absorbing boundaries, where the concentration begins to drop at a distance of about  $2r_g^0$ . Consideration of larger statistical weights to be assigned to configurations close to the boundary suffices to explain



**Figure 3** (a) Chain generation process: from an initial direction  $AO$  three directions  $OC$ ,  $OF$  and  $OG$  are allowed, forming an angle of  $109.5^\circ$  degrees with  $AO$ . The length of each side of the cube (e.g.  $AB$ ) has been taken equal to 2. (b) In reflecting boundary statistics there is one or more than one way to generate a given configuration. For configuration  $AB$ , lying at the centre of the boundary there is only one way. For configuration  $CD$  there is the direct way or after reflection on the boundary at one or several of the points  $E$ ,  $E'$ ,  $E''$

this difference in behaviour. However, as shown later, the configurational entropy change  $\Delta S$  from the free (unbounded) chain varies now as the inverse first power of the characteristic length of the boundary, instead of varying as the inverse second power, as is the case for absorbing boundaries. This is a result of some practical interest. Thus, two features that distinguish absorbing from reflecting boundary statistics are: (a) different concentration profiles and (b) different power laws for the entropy change  $\Delta S$  with the characteristic length  $R$  of the boundary.

However, since the thermodynamics of confined chains is considered to have been solved through consideration of absorbing boundaries and use of the diffusion equation<sup>1,2</sup>, the question now arises: why is it useful to consider the Monte-Carlo statistics of reflecting boundaries? To answer this question some detailed arguments are developed below. First of all, a sequence of  $N$  steps inside the boundary can be interpreted in two ways: it may be considered to be, as previously, a particular configuration of a single macromolecule of index  $N$ ; an alternative interpretation would be that these steps represent the random motion of an ordinary, simple molecule inside the network during a time  $d\tau_N$ , with the restriction that backward motion, when a step is completed, is prohibited. Such a motion certainly preserves the general statistical features of Brownian motion, even though backward motion is not permitted.

These two alternative interpretations will be called for convenience SMC (single macromolecular chain) and SSM (steps of a simple molecule). Now it is almost evident that in the SSM interpretation absorbing boundary statistics cannot be retained. This is so because, for such statistics the concentration profile inside the boundary (=the sphere) is a function of the number of steps  $N$  or, alternatively, the time  $d\tau_N$  during which the trajectory of the simple molecule is followed. As  $N$  increases, the relative density of steps increases at the centre of the

sphere while at the same time the decrease in density as one goes to the periphery becomes more steep. Such a situation is, however, nonphysical, since the mean density of a gas inside a vessel is a constant and does not depend on time. Due to the ergodic theorem, as  $N \rightarrow \infty$ , the density of steps of a simple molecule should also be a constant. As shown in the Results and Discussion section, reflecting boundary statistics ensure constancy of the density of steps inside the boundary, and therefore reflecting boundary statistics should be used in the case of simple molecules. Let us now turn to the SMC interpretation of  $N$  steps. In this case, the situation seems more complicated, and two cases have to be distinguished,  $R \gg r_g^\circ \sim N^{1/2}$  and  $R < r_g^\circ$ , with a transition region probably in the vicinity of  $R \simeq 2r_g^\circ$ . For  $R \gg r_g^\circ$ , since for entropic reasons a macromolecule cannot be flattened against the wall of the boundary (=no attractive energy term in our problem), it seems reasonable to assume that the mean concentration of segments should fall, beginning at a distance of the order of  $2r_g^\circ$  from the boundary. Such a concentration profile is consistent with absorbing boundary statistics.

If  $R < r_g^\circ$ , we can make the following arguments: consider first that we are in the SSM situation, where a number  $N$  of simple molecules move inside the vessel in a random fashion. The mean density of molecules (or steps) inside the vessel is then a constant. Due again to the ergodic theorem, if we wait for a sufficient length of time, the  $N$  simple molecules will find themselves in such a topological configuration as to be linked at an instant  $t$  by  $N-1$  links of equal length. Assuming that some Maxwell's demon is able to perform instantaneously the desired linkage, we now have a single molecule of  $N$  steps, and we go abruptly from a SSM to a SMC situation. Does this also mean that at the same time we should abruptly shift from RB statistics (the only relevant for simple molecules) to AB statistics? If this were so, the concentration profile inside the sphere should shift from the

horizontal straight line A of Figure 1 to curve B of the same Figure. This means that as a result of the linkage, some centripetal force should be at work, acting on the chain segments. Since, however,  $R < r_g^\circ$ , how such a force may arise from the linking is hard to imagine, at a time where the chain 'strives' to recover its unperturbed dimensions which are  $r_g^\circ > R$ . In such a situation, one would intuitively think that the mean segment density is a constant within the vessel except at the closest vicinity of the boundary, and if this were so, reflecting boundary statistics should be used.

The above argument is of course qualitative and by no means constitutes proof that, for  $R$  of order  $r_g^\circ$ , reflecting boundary statistics should be used for polymeric substances, as is always the case for simple molecules.

Ultimately, experience should determine whether boundaries act on confined chains in an absorbing or in a reflecting way, depending in particular on the relative dimensions  $R$  and  $r_g^\circ$ , with probably, a compromise between the two modes in the vicinity of  $R \approx 2r_g^\circ$ . It is our desire to ensure that the reader will not conclude that our argument is that confined chains obey RB rather than AB statistics, in all physical situations; rather, our argument is that AB statistics do lead to some difficulties, especially for small confining volumes, which deserve at least a closer examination. Pending such an examination, which lies beyond the scope of the present article, we give, in the following, the Monte-Carlo statistics of both absorbing and reflecting boundaries in the hope that these might constitute an element in the closer examination of the problem raised above.

## COMPUTATIONAL TECHNIQUES

For convenience, the boundary considered in the calculations to follow will be a sphere whose radius  $R$  can be varied.

Generation of statistical chains inside the sphere and calculation of the different parameters of these chains have been performed by using a Monte-Carlo method. The program has been written in FORTRAN, partially using double precision calculations and was run on a Computer Automation LST2 minicomputer with 32 kwords of 16 bits. Random numbers were generated using a method exposed elsewhere<sup>6</sup>, and proved to be sequence-free and well distributed over the range 0, 1.

The radius of the sphere, the number of monomeric units  $N$  of the chain and the number of chains generated during each run were the only input data.

### Generation of statistical chains

A random walk in a body-centred cubic lattice is performed: if the coordinate axes are colinear with the lattice edges, the vector defining a given segment of the chain is written  $(a, b, c)$ ,  $a$ ,  $b$  and  $c$  being equal to +1 or -1, the lattice edge being equal to 2 and the step length equal to  $3^{1/2}$ . When going from one segment to the following, three different directions are allowed, each of them corresponding to changing the sign of one of the coordinates of the previous vector (Figure 3). The chain thus generated is equivalent to a polymethylene macromolecule.

### Determination of the various parameters of the system

The following parameters and their distribution have been calculated:

(1) The distributions of the end-to-end distances, the root-mean-square (r.m.s.) end-to-end distance and its standard deviation.

(2) The distributions of the centres of gravity from the centre of the sphere and the mean distance of the centres of gravity from the centre of the sphere.

(3) The distribution of the radii of gyration  $r_g$  and the r.m.s. value  $\langle r_g^2 \rangle^{1/2}$  given respectively by:

$$r_g = \left[ \frac{1}{N} \sum_{j=1}^N \sum_{i=1}^z (x^{ij} - x_g^i)^2 \right]^{1/2} \quad (1)$$

and

$$\langle r_g^2 \rangle^{1/2} = \left[ \frac{\sum_{i=1}^n r_{gi}^2}{n} \right]^{1/2} \quad (2)$$

where  $n$  is the number of chains generated and  $x^{ij}$  and  $x_g^i$  respectively the coordinates of segment  $j$  and of the centre of gravity.

(4) The mean number of rebounds  $\langle B_1 \rangle$  and  $\langle B_2 \rangle$  and the distribution of the sum  $\langle B \rangle = \langle B_1 \rangle + \langle B_2 \rangle$  as a function of  $R$  (see Theory, Reflecting Boundary Statistics).

(5) The mean number of deadlocks  $\langle C_1 \rangle$  and  $\langle C_2 \rangle$  as a function of  $R$  (same remark as above).

(6) The number of deadlocks  $D$  (three steps back to continue) (same remark as above).

## THEORY

### Absorbing Boundary Statistics

In Absorbing Boundary Statistics (ABS) a configuration being generated is discarded as soon as one of its steps crosses the boundary; if no step crosses the boundary, the obtained configuration is retained as an element of the Monte-Carlo statistics. Since all configurations retain equal statistical weights as in the case of a free chain, the entropy change of the confined chain with respect to that of the free chain is given simply as

$$\Delta S = k \ln(n/n_{tot}) \quad (3)$$

where  $n$  is the number of chains retained for the Monte-Carlo statistics while  $n_{tot}$  is the total number of trials of the computer (retained + discarded trials).

Here is perhaps the place to stress once more that an absorbing boundary, as defined above, should not be confused with an adsorbing interface. Adsorption involves free energy changes, that is energetic as well as entropic interactions between chain and interface, the latter being given by equation (3) if AB statistics are obeyed and by equation (7) if RB statistics are obeyed. Neither of equations (3) or (7) contains an energetic term, which is, however, always present in adsorption phenomena.

### Reflecting Boundary Statistics

As previously indicated, in Reflecting Boundary Statistics (RBS), when, during the chain generation process, a step crosses the boundary, the corresponding configuration is not discarded, as is the case in ABS; instead it is allowed to continue, by ordering the computer to choose another direction, after taking one or, if necessary, more than one step back. For the body-centred cubic lattice used in this work, there are essentially two

types of interactions (or events) between a chain being generated in the network and the boundary: these events are respectively called 'rebounds' and 'deadlocks' and are examined in more detail below.

**Counting of the rebounds and deadlocks.** A 'rebound' is considered to occur if the random walk leads to a lattice point situated outside the sphere and if generation of the chain can continue after coming back one step and choosing another permitted direction. The computer counts separately as  $B_1$  and  $B_2$  events the occurrence of one or two possible directions after coming back one step, the third direction of course, that leading to the rebound, being excluded. If it is not possible to continue after one step back (all three possible directions being forbidden as leading to rebounds), we have a 'deadlock'; no rebound is then registered and the computer is ordered one step further back. The program then checks the possibility of continuing over the two next steps, counting separately as  $C_1$  and  $C_2$  the possibilities of continuing in one or two directions at the first step forwards, the third direction being excluded as leading to the deadlock. After a  $B_2$  or  $C_2$  event, there is a random choice by the computer of the direction to be followed. It sometimes happens that three steps back are needed to continue the chain generation process, all directions after two steps back leading to a deadlock. These so-called  $D$  events are scarce and have not been taken into account in the calculations to follow, as their contribution is negligible.

**Sampling.** Two series of experiments with  $N=100$  and  $N=1000$  have been performed. The Monte-Carlo sampling comprised between 50 and 10 000 chains, depending on the statistics and  $R$ , but usually 500 or 1000 chains. Only the results for  $N=1000$  are quoted here as the results for  $N=100$  contribute nothing new for the purpose of this work.

**Configurational entropy of the chain.** Let a chain of index  $N$  be enclosed inside a sphere of radius  $R$ , the boundary of the sphere acting on the chain in a reflecting fashion. To calculate the entropy of the chain, we assume first that for  $R$  being infinite (free chain) the number of configurations of the chain is  $3^N$ . For  $R$  being finite, let us assume that a given configuration displays events of types  $B_1, B_2, C_1$  and  $C_2$  in numbers per step equal to  $b_1, b_2, c_1$  and  $c_2$ . Suppose that at the  $i$ th step ( $i < N$ ) a  $B_2$  or  $C_2$  event occurs. We assume now that any of the two permitted paths, if followed, will lead *in the mean* to the same number of events of the various kinds until completion of the chain. In other words we assume that there is no correlation between the path followed after an event has occurred and the number of events of the various kinds to follow. With this assumption, the number of configurations of all chains displaying events of kind  $B_1, B_2, C_1, C_2$  in numbers per segment  $b_1, b_2, c_1, c_2$  is

$$Z = 3^{N(1 - (3b_2 + 1.5b_1 + c))} \times 2^{N(3b_2 + 1.5c_2)} \quad (4)$$

where  $c = c_1 + c_2$ . To obtain the above relationship, one may observe that all configurations displaying a total of  $Nb_2$  rebounds of kind  $B_2$  (two possible directions after one step back) will have in the mean  $3Nb_2$  positions which may potentially generate a  $B_2$  event. But each of these positions has only two possible directions, so that, instead of having  $Z = 3^N$  we shall have  $Z = 3^{N(1 - 3b_2)} \times 2^{3Nb_2}$  configurations; one further observes that for configurations displaying a total of  $Nb_1$  events  $b_1$  (one possible

direction after one step back) there are in the mean  $1.5Nb_1$  positions which may potentially generate a  $B_1$  event. But each of these  $1.5Nb_1$  positions has one possible direction for the continuation of the chain, so that  $Z$  is further reduced to  $Z = 3^{N(1 - 3b_2 - 1.5b_1)} \times 2^{3Nb_2}$ . Finally reasoning in the same way for  $C$  events, equation (4) is obtained. In the above equation we have neglected the statistical fluctuations between potential event-generating positions and the actual number of events occurring. The entropy of all configurations displaying the set of events  $B_1, B_2, C_1, C_2$  in numbers  $Nb_1, Nb_2, Nc_1, Nc_2$  is

$$S(Nb_1, Nb_2, Nc_1, Nc_2) = kN \{ [1 - (3b_2 + 1.5b_1 + c)] \ln 3 + [3b_2 + 1.5b_1] \ln 2 \} \quad (5)$$

where  $c = c_1 + c_2$ . Let now  $P(Nb_1, Nb_2, Nc_1, Nc_2, R)$  be the probability of the configurations displaying events  $B_1, B_2, C_1, C_2$  in numbers  $Nb_1, Nb_2, Nc_1, Nc_2$  for the value  $R$  of the radius of the enclosing sphere. Then, the configurational entropy of the chain for all possible configurations within the sphere is, with the assumption of uncorrelated events:

$$S(R) = \iiint P(Nb_1, Nb_2, Nc_1, Nc_2, R) \times S(Nb_1, Nb_2, Nc_1, Nc_2, R) db_1 db_2 dc_1 dc_2 \quad (6)$$

Equation (5) shows that  $S(Nb_1, Nb_2, Nc_1, Nc_2)$  is a linear function of the number of events  $B_1, B_2, C_1$  and  $C_2$ . As a result of this only marginal probabilities occur inside the integrand and one obtains

$$S(R) = kN \{ [1 - \langle 3b_2(R) \rangle + \langle 1.5b_1(R) \rangle + \langle C(R) \rangle] \ln 3 + [\langle 3b_2(R) \rangle + \langle C_2(R) \rangle] \ln 2 \} \quad (7)$$

where the brackets stand for 'mean value'. Thus, to calculate the entropy of the chain, only the mean number of the various events is needed and not their probability distribution.

The entropy difference  $\Delta S(R_1, R_2)$  for two values  $R_1$  and  $R_2$  of the enclosing sphere is obtained from equation

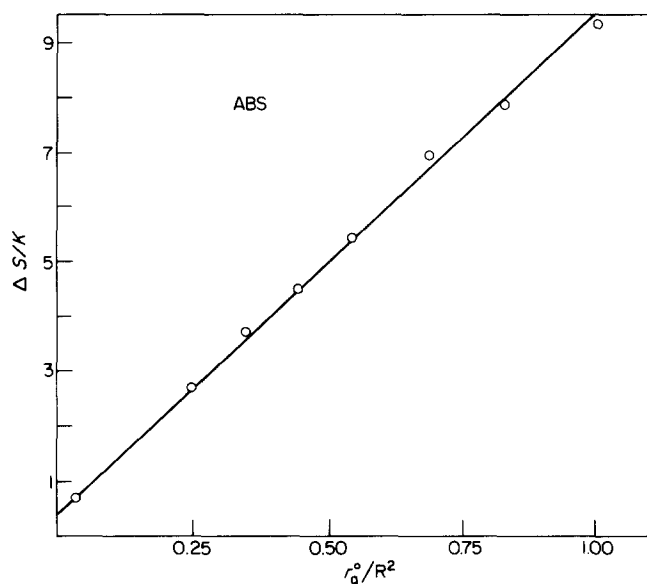


Figure 4 Entropy variation from the free (unbounded) state of the chain as a function of  $R^{-2}$ , where  $R$  is the radius of the confining sphere, when the boundary is considered to be absorbing

(7) by replacing  $R$  by  $R_1$  and  $R_2$  and making the difference. In particular

$$\Delta S(\infty, R) = kN \left\{ -[\langle 3b_2(R) \rangle + \langle 1.5b_1(R) \rangle + \langle C(R) \rangle \ln 3] + [\langle 3b_2(R) \rangle + \langle C_2(R) \rangle] \ln 2 \right\} \quad (7')$$

The mean numbers  $\langle Nb_1 \rangle$ ,  $\langle Nb_2 \rangle$ ,  $\langle Nc_1 \rangle$  and  $\langle Nc_2 \rangle$  which are registered by the computer merely describe the specificities of the body-centred cubic lattice we used. The absolute values of the entropies per chain or per chain segment also reflect this specificity. For  $R = \infty$ , these entropies are respectively  $kN \ln 3$  and  $k \ln 3$ . However, the entropy difference for two different  $R$  values (or, alternatively, the ratio of conformations) should be a universal function of  $R$ , independent of the particular network used to generate the chain. We make therefore the fundamental assumption that the entropy difference obtained using a body-centred cubic lattice also describes the entropy difference for other chain generating processes and in particular the random flight statistics considered by Casassa<sup>1</sup>. This author has derived the following expression for the partition  $K$  of statistical chains inside a sphere and in the infinite medium outside it:

$$K_{\text{sphere}} = \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp \left\{ -m^2 \pi^2 \frac{\langle r_g^2 \rangle}{R^2} \right\} \quad (8)$$

The configurational entropy difference  $\Delta S$  between free chains outside the sphere and confined chains inside the sphere is given by

$$\Delta S = k \ln K \quad (9)$$

Inspection of equation (8) shows that the second term of the series is less than one thousandth of the first as soon as  $R$  is less than  $3\langle r_g^2 \rangle^{1/2}$  and becomes negligibly small for  $R$  values less than  $\langle r_g^2 \rangle^{1/2}$ . Therefore, the entropy difference per segment between two values  $R_1$  and  $R_2$  less than  $3\langle r_g^2 \rangle^{1/2}$  is given by

$$\Delta S/kN = -\pi^2(R_1^{-2} - R_2^{-2}) \quad (9)$$

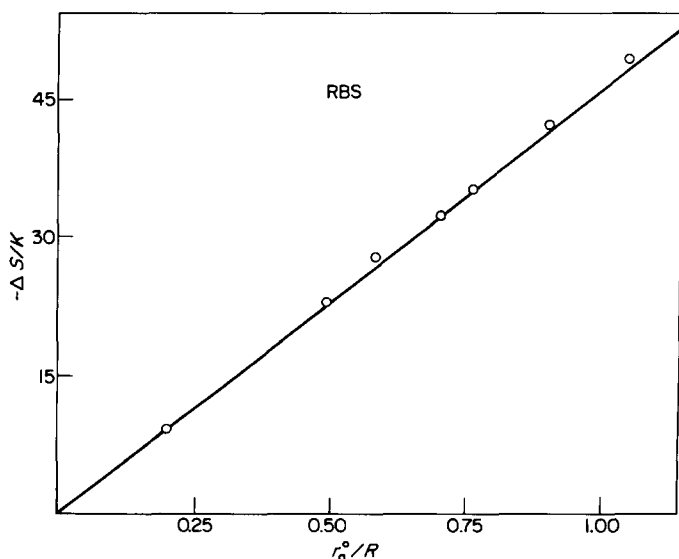


Figure 5 Entropy variation from the free (unbounded) state of the chain as a function of  $R^{-1}$ , where  $R$  is the radius of the confining sphere, when the boundary is considered to be reflecting. For the large values of  $R^{-1}$  there is an upwards trend of the Monte-Carlo points from the straight line of the figure which is not shown

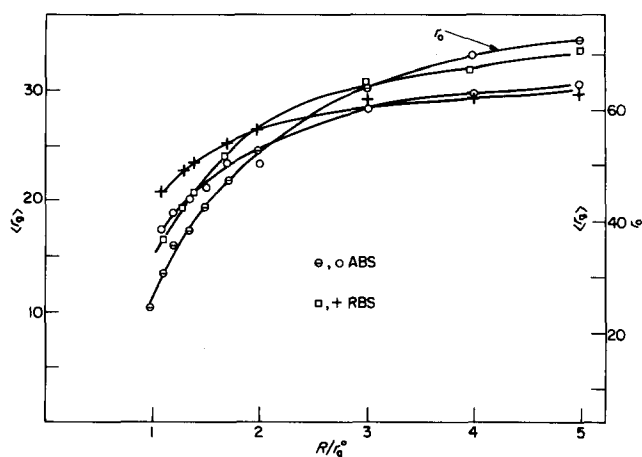


Figure 6 Mean radius of gyration  $\langle r_g \rangle$  and root-mean-square end-to-end distance  $r_0$  for absorbing and reflecting boundary statistics as a function of the ratio  $R/r_g^0$ , where  $R$  is the radius of the enclosing sphere and  $r_g^0$  the unperturbed radius of the chain. For the large values of  $R/r_g^0$ , the corresponding values are larger for ABS, whereas for the small values of  $R/r_g^0$  the inverse phenomenon is observed

Thus, Casassa's equation implies that  $\Delta S(\infty, R)/kN$  should be proportional to  $R^{-2}$ . The computer results given in the next section show that indeed for absorbing boundary statistics  $\Delta S$  varies as  $R^{-2}$  (Figure 4). On the other hand, reflecting boundary statistics lead through equation (7) to a variation law in  $R^{-1}$  (Figure 5). One can conclude that Casassa's equation and use of the diffusion equation corresponds to absorbing boundary statistics. However, as was suggested earlier, statistical chains may not obey absorbing boundary statistics in all the  $R$  range, and in particular for  $R$  values less than  $3r_g^0$ . For this reason, in the next section Monte-Carlo calculations for various parameters of statistical chain resulting from both AB and RB statistics are given.

## RESULTS AND DISCUSSION

In Figures 1 and 2 the concentration profiles as a function of  $r/R$  ( $r$  = distance from the centre of the sphere) for AB and RB statistics are given. It can be seen from the two selected values of  $R$ ,  $R = 5r_g^0$  and  $R = 1.1r_g^0$ , that the general pattern does not change with  $R$ : for RB statistics the concentration remains constant inside the sphere and drops only in the vicinity of the boundary; for ABS, as long as  $R \geq 3r_g^0$ , there is a plateau region in the central region of the sphere and then the concentration drops at a distance of the order  $2r_g^0$  from the boundary. If  $R$  is less than  $\sim 2r_g^0$ , the plateau region disappears, the concentration of segments is maximum at the centre of the sphere and then drops monotonously to a zero value at  $r = R$ . In Tables 1 and 2 are given as a function of  $R/r_g^0$  the values of  $\langle r_g \rangle$ ,  $\langle r_0 \rangle$  (the root-mean square end-to-end distance) and their standard derivations.

In Figure 6,  $\langle r_g \rangle_{\text{ABS}}$ ,  $\langle r_0 \rangle_{\text{ABS}}$  and the corresponding quantities for RB statistics are plotted.

As already observed, Figures 4 and 5 show that  $\Delta S_{\text{ABS}}$  varies as  $R^{-2}$  while  $\Delta S_{\text{RBS}}$  varies as  $R^{-1}$ . Though this result, obtained here for statistical chains, cannot be directly generalized to usual polymeric chains, one may infer that for the latter chains also the dependence of  $\Delta S$  on  $R$  may follow different laws, depending on the type of statistics being obeyed in the particular case considered.

**Table 1** Absorbing Boundary Statistics ( $N = 1000$ ,  $r_g^0 = 31.623$ ,  $r_0^0 = 77.460$ )

$R/r_g^0$	Monte-Carlo sampling	$r_g$	Standard deviation	$r_0$	Standard deviation	$\Delta S/k$
5.00	10 000 <sup>a</sup>	30.30	7.20	73.09	28.817	0.733
4.00	500	29.75	7.06	70.79	28.45	0.941
3.00	500	28.18	5.90	64.43	25.32	1.433
2.00	500	24.70	4.33	53.20	20.11	2.719
1.70	500	23.29	3.71	47.55	16.95	3.687
1.50	500	21.02	3.04	42.83	15.75	4.526
1.35	500	20.03	2.69	38.16	14.14	5.425
1.20	500	18.50	2.04	36.05	13.16	6.894
1.20	500	18.66	1.95	36.35	12.48	—
1.10	50 <sup>b</sup>	17.33	1.78	31.00	11.49	7.895
1.00	50	15.85	1.77	24.60	5.87	9.372

<sup>a</sup> Sampling increased in order to have a good concentration profile inside the enclosing sphere

<sup>b</sup> Sampling reduced to save computational time

**Table 2** Reflecting Boundary Statistics ( $N = 1000$ ,  $r_g^0 = 31.623$ ,  $r_0^0 = 77.460$ )

$R/r_g^0$	$r_g$	Standard deviation	$r_0$	Standard deviation	Monte-Carlo sampling
5.00	29.78	7.18	70.76	27.97	10 000 <sup>a</sup>
4.00	29.05	6.88	66.65	26.46	1000
3.00	28.62	6.84	65.42	26.05	1000
2.00	26.27	5.59	56.52	21.12	1200
1.70	25.10	5.32	52.00	19.83	1200
1.40	23.32	4.17	45.21	16.38	1200
1.30	22.69	3.83	43.13	15.44	1200
1.10	20.76	3.12	36.86	12.38	1200
0.95	19.05	2.34	31.94	10.73	1200
0.85	17.59	1.91	28.63	9.95	1200
0.75	16.04	1.44	24.84	8.49	1200
0.65	14.28	1.05	21.62	7.56	1200
0.55	12.36	0.70	18.28	6.27	1200
0.45	10.27	0.42	14.78	5.16	1200
0.35	8.07	0.23	11.25	3.85	1200

<sup>a</sup> Sampling increased in order to have a good concentration profile inside the enclosing sphere

**Table 3** Reflecting Boundary Statistics (number of rebounds  $b_1$  and  $b_2$  and deadlocks  $c_1$  and  $c_2$  per segment as a function of  $R$ ; entropy change  $\Delta S$  as a function of  $R$ )

$R/r_g^0$	$b_1 \times 10^3$	$b_2 \times 10^3$	$c_1 \times 10^4$	$c_2 \times 10^4$	$d \times 10^5$	$-\Delta S/k$
5.00	2.43	4.20	0.06	1.68	0.25	9.19
4.00	3.00	5.05	0.19	1.68	0.20	11.18
3.00	4.26	6.87	0.47	2.13	0.50	15.52
2.00	6.34	10.23	1.86	2.82	1.58	23.21
1.70	7.51	12.51	2.37	4.02	3.17	28.02
1.40	8.77	14.63	2.89	4.04	5.58	32.72
1.30	9.49	15.66	3.53	4.14	4.83	35.24
1.10	11.77	18.33	4.10	5.52	7.50	42.36
0.95	13.69	21.37	5.44	6.97	9.33	49.43
0.85	15.39	23.36	6.49	6.49	8.92	54.76
0.75	17.98	26.35	6.72	7.16	11.42	62.73
0.65	20.71	31.08	8.95	9.45	12.83	73.31
0.55	25.04	36.33	10.75	10.80	15.92	87.08
0.45	30.68	44.01	16.69	16.76	26.85	106.60
0.35	44.68	52.55	25.73	25.66	40.00	203.47

This is of importance in several problems arising in polymer science. To mention a few:

- (i) Polymer chains enclosed inside voids of various forms (spheres, ellipsoids, cylinders) or confined by slabs.
- (ii) Gel permeation chromatography.
- (iii) Collapse of polymer chains.
- (iv) Polymerization inside microemulsions<sup>7</sup>.

In the latter case, the unperturbed dimensions of the chains polymerized inside inverse micelles may exceed by a factor of up to 10 the radius of the core of the inverse micelle<sup>8</sup>, so that the polymerized chain is in a quite collapsed form. Following the argument developed in this article, the entropy of such chains should obey RB rather than AB statistics.

We may now further comment on *Figures 1* and *2* as follows: a chain enclosed inside a void will in general (neglecting for present purposes any energetic effects) take such configurations as will maximize its entropy. When  $R \gg r_g^0$ , the configurations maximizing the entropy are those lysing far from the boundary, so that in this case AB statistics are probably correct, and the concentration profile should be that of curve B of *Figure 1*. On the other hand, when  $R \approx r_g^0$ , AB statistics concentrate the segments at the centre of the sphere, and such configurations probably do not maximize the entropy. Rather one would

think that in this case the chain tends to occupy any available space, in which case the segments of the chain will be evenly distributed inside the void. This implies that RB statistics are now obeyed. The above comment summarizes the argument developed under 'General Considerations' earlier, following which a chain enclosed inside a sphere (and more generally a void) should obey AB statistics as long as  $R \gg r_g^0$  and should shift to RB statistics as soon as  $R \sim 2r_g^0$  or less, with presumably, an intermediate region between the two where the kind of statistics obeyed is not clearly defined and is some sort of compromise between the two.

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