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Concentration profiles of confined chains having absorbing and reflecting statistics

Alain Jaeckel
Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France

and Jean Dayantis*
Science des Matériaux Vitreux, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex, France
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After recalling the two step-by-step chain-generation procedures of long chains used in Monte Carlo simulations, which lead respectively to absorbing and to reflecting statistics, a suggestion is made regarding the statistics to be considered when polymer chains are confined. According to this suggestion, which originates in the respective shapes of the chain-step concentration profiles, there is in good solvents a shift of statistics from absorbing to reflecting, when the dimensions of the bounding surface become comparable to or smaller than those of the free (non-confined) chain. Copyright © 1996 Elsevier Science Ltd.

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In a previous paper[1], the two step-by-step computer chain-generation procedures of uncorrelated self-avoiding walks (SAWs) or random-flight walks (RFWs) were described in detail. In the first procedure, for free (unbounded) chains, any initiated chain which encounters an already-visited lattice site is discarded from the Monte Carlo (MC) sample. In the second procedure, when this happens, the computer is asked to take another direction, if available, where no such double occupancy will occur. The first procedure, pioneered by Wall and co-workers[2,3], leads to absorbing statistics (AS). The second procedure, introduced by Rosenbluth and Rosenbluth[4] and then 'rediscovered' on several occasions[5,6], leads to reflecting statistics (RS). The attrition, i.e. the probability of failure of an initiated chain, is always much larger in AS than in RS. Hence, the latter statistics have often been used in order to save computational time. However, in RS, the possible N-step configurations are not obtained with the same probability by the computer. Therefore, to revert to the 'natural' AS, each chain j in the MC sample obtained using RS has to be weighted by a proper weighting factor w_j. The resulting weighted reflecting statistics (WRS) is essentially equivalent to AS[7,8].

The foregoing considerations are valid whether the chains are free in space (unbounded), or constrained to lie inside some boundary of arbitrary shape. However, for free RFWs (i.e. chains with no excluded volume) there is no point in distinguishing between AS and RS. If the RFWs are constrained to lie inside a given volume, the distinction arises due to the boundary: in AS, any chain crossing the boundary is eliminated from the MC sample; in RS, on the other hand, the computer is ordered one step back to look for another direction for which no crossing of the boundary occurs. In practice, the computer screens one or several steps ahead for permitted directions, and then chooses one of these with equal probability[8]. (In the present work, the screening was made one step ahead. Meirovitch[9] has examined the case of screening many steps ahead.)

Some years ago[10], step-concentration profiles for N-step RFWs confined inside spheres of varying diameter were given. Depending on the statistics considered, AS or RS, the step-concentration profiles were very different. In AS, as soon as $\rho_0 = R/ < r >$, where R is the radius of the sphere and $< r >$ is the mean end-to-end distance of the free chain, becomes small enough ($\rho_0 <$ about 1.5), chain steps tended to concentrate at the centre of the sphere, the vicinity of the sphere surface being almost step-free. In RS, the step-concentration profile remained flat, whatever the ρ_0 value. Now, at least for polymer chains dissolved in good solvents, due to the osmotic pressure generated by the density gradient, one expects that when ρ_0 is small enough, chain steps will seek to occupy all available volume. In other words, it seems that in this case RS might be a better description of the physical situation than AS. Therefore, the suggestion was made[10] that, for polymer chains dissolved in good solvents, there is a gradual shift in the statistics obeyed from AS to RS, as the ρ_0 value decreases from about two to about one.

In the present communication, we extend previous work by investigating the behaviour of confined SAWs. These are certainly a better model for real polymer chains than the previously considered RFWs. To this end, N-step SAWs have been computer-generated on a simple cubic lattice inside spheres of varying diameter, each confined lattice site having the same probability of being the starting point of an initiated chain. The sphere of diameter R was divided into an arbitrary number (up

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* To whom correspondence should be addressed. Permanent address: Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France

to 22) of spherical shells of the same width, and the number of chain-steps falling inside each spherical shell in the whole MC sample recorded. This number was then divided by the number of lattice sites inside each shell, to ensure a consistent determination of the step concentration[11,12]. For convenience, we reproduce in *Figure 1* a few concentration profiles for AS, published elsewhere[1]. In *Figure 2*, we show concentration profiles for RS, for chains of various length, confined inside a sphere of $R = 10$, divided into 10 spherical shells of equal width. The concentration profiles are flat inside almost all of the spherical volume. The drop of concentration which appears near the surface of the confining sphere is an artefact due to the finite size of the lattice array. A small 'hump' is apparent near the penultimate spherical shell for the shorter chains. The effect disappears for the longer chains. This effect may be explained as follows: shorter chains generated near the boundary are reflected and will occupy the spherical shells nearest to the boundary. When larger chains are reflected, steps of the growing chain can occupy all spherical shells, and therefore the effect disappears. In summary, the step-concentration profiles of SAWs confined inside a spherical boundary are flat for RS, whatever the value of the reduced radius ρ_0 of the confining sphere. Thus, there are distinctive behaviours of the concentration profiles for AS and RS of SAWs, a result which generalizes that found previously for RFWs. We can then extend to SAWs our previous suggestion of a shift of statistics from AS to RS as ρ_0 is decreased. Of course, there is not sufficient evidence to conclude that a real polymer chain will strictly obey RS when the confining volume becomes small with respect to the free dimensions of the chain. We simply suggest that it looks as though RS constitutes a better description of physical reality than AS in this case.

Physically, the suggested change in statistics may be viewed as follows. Consider a chain dissolved in a good solvent and enclosed inside some boundary. When the dimensions of the boundary with respect to those of the free chain are small enough, most allowed configurations will display many 'contacts' with the boundary, and will bounce back and forth on the boundary. Therefore such configurations will have more chances to repeat themselves than configurations primarily evolving near the central part of the bounding surface, with no or few contacts with the boundary. The latter, relaxing through thermal motion, will tend to occupy as much space as possible, and therefore will in general evolve towards configurations displaying many 'contacts' with the boundary. Only scarcely will these configurations spontaneously evolve to configurations with few or no 'contacts' with the boundary. The net effect of the boundary, neglecting fluctuations, will then be to equalize the step density inside the boundary.

A natural extension of the present work is to check experimentally that the segment density of chains dissolved inside microdroplets is nearly constant inside the boundary. On the theoretical side, a statistical mechanical analysis of the trajectory of confined chains in phase space should be performed. Both these extensions lie beyond the scope of the present investigation.

Preliminary results of work in progress using MC simulations, which lie outside the scope of the present communication, show that the pressure exerted by an isolated chain on the boundary depends on the statistics considered. Therefore, if our suggestion of a gradual change of statistics from AS to RS in the range $\rho_0 = 2$ to $\rho_0 = 1$ is correct, this should be of practical interest. For example, in microemulsion polymerization[13], the thermodynamic stability of the microemulsion after polymerization will depend on the surface tension of the microdroplets containing the polymerized material. This in turn will depend, as one factor among others, on the pressure exerted by the polymerized material on the confining volume, i.e. on the continuum in which the microdroplets are dissolved or suspended (depending on whether there is thermodynamic stability or not).

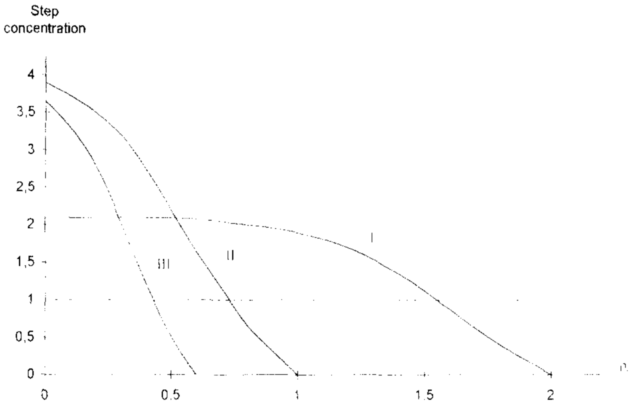

Figure 1 Chain-step density profiles for absorbing statistics for a chain of 58 steps confined inside spheres of reduced radii $\rho_0 = R / < r >$ (R, radius of the sphere; $< r >$, mean end-to-end distance of the free chain): curve I, $\rho_0 = 2$; curve II, $\rho_0 = 1$; curve III, $\rho_0 = 0.6$. The straight line corresponds to the uniform distribution of chain steps inside the sphere. As this uniform distribution for a given sample size in inversely proportional to the confined volume, it follows that actual densities will be obtained by multiplying the displayed densities by $\rho_0{}^3$. Sample size equal to 5.8×10^6 chain-steps

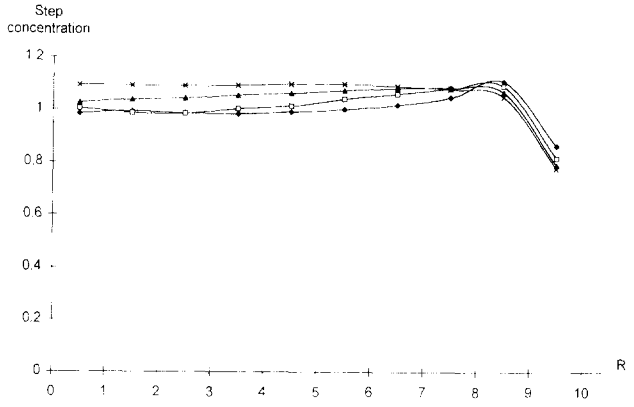

Figure 2 Chain-step density for reflecting statistics for chains of various lengths confined inside a sphere of radius $R = 10$. The sphere is divided into 10 spherical shells of equal width. Contrary to what happens in absorbing statistics, the concentration profiles are almost flat and do not depend on ρ_0, the relative linear dimensions of the confining sphere and the free chain. The drop in concentration seen near the surface of the sphere is a computational artefact. The small 'hump' appearing near the penultimate spherical shell may be explained, for short chains, as being due to reflection of these chains by the boundary, the remaining segments of the chains fitting the shells nearest to the boundary. This phenomenon, responsible for the fact that the concentrations inside the sphere are not strictly equal for all chain lengths, vanishes for larger chains. ◆, 6 steps; □, 20 steps; ▲, 48 steps; ×, 90 steps

Pressure results for AS have been published elsewhere[14,15]. Pressure results for RS are forthcoming.

In conclusion, it is almost certain that there is a range of reduced radius ρ_0 in which AS cannot apply. Hence the suggestion made here deserves further consideration, before being accepted as correct or useful, or discarded as irrelevant.

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