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Fixed-scale transformation approach to linear and branched polymers

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Abstract. The radius exponent of two- and three-dimensional self-avoiding walks and branched polymers are computed in the fixed-scale transformation framework. The method requires the knowledge of the critical fugacity k_c, but from this non-universal parameter it is possible to compute the universal critical exponent. The results obtained are within 1% of exact or numerical values. This confirms the versatility and quantitative power of this new theoretical approach and gives the opportunity to provide a discussion of the analogies and differences between the real space renormalization group and the fixed-scale transformation method.

1. Introduction

Scaling concepts and renormalization group ideas have been applied with increasing efforts and stimulating successes in describing the critical properties of polymers [1–3]. There are two main different classes of polymers: linear and branched. In the presence of a good solvent the statistics of long and isolated linear molecules is equivalent to the statistics of a self-avoiding walk on a lattice (SAW). If the constituent monomers have three or more functional groups, branched molecules can form and the statistics of such polymers is more complex and usually described by lattice animals (LA) models. These systems have the asymptotic properties of self-similarity when considered at their critical point, i.e. in the limit of infinitely long chains. Here the aggregates can be geometrically characterized by a fractal dimension D. The fixed-scale transformation (FST) [4], is an analytical approach to fractal growth problems. This method focuses on the distribution of elementary configurations appearing in the fine- (coarse-) grained description of the process. For this distribution an iterative transformation is derived on the basis of the dynamical growth rules at a given fixed scale. Even if originally conceived as an approach to dynamic growth problems, FST can be adapted to the study of equilibrium critical phenomena like percolation [5]. When considering critical equilibrium problems, and specifically linear and branched polymers, in a grand canonical context, the self-similarity of the systems is automatically guaranteed by fixing the step fugacity at its critical value. The fact that the critical properties of linear and branched polymers are relatively well known gives us the opportunity to understand more deeply the analogies and the differences between the real-space renormalization group (RSRG) and FST approaches. In this context the FST results can be compared with either exact or extremely accurate estimates by several methods [6–9]. Our best estimates of the correlation length exponent for two- and three-dimensional SAW and for LA, are always within 1% of the expected values. These results show a good convergence with schemes of

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calculation of increasing complexity. This suggests that the agreement is not coincidental as may often be the case in real space renormalization group approaches.

The paper is organized as follows: in section 2 the FST method is schematically reviewed and rephrased in view of its application to critical equilibrium problems; in sections 3 and 4 we present the application of this analytical approach to two- and three-dimensional SAW and to lattice animals; section 5 contains the summary and the discussion of the results.

2. The fixed-scale transformation for critical equilibrium problems

The FST approach has been developed with fractal growth problems such as DLA and DBM [10, 11] in mind; i.e. for intrinsically non-equilibrium models. However, this method can also be applied to the fractal description of equilibrium problems such as percolation and Ising and Potts clusters [12]. The FST method starts with the identification of the elementary configurations necessary to define the coarse- (fine-) graining process. Here the intersection of the fractal structure with a line perpendicular to the growth direction is considered. For the study of equilibrium fractal structures, this direction is arbitrarily chosen. We conventionally refer to this direction as the 'growth' one. For the fractal structure embedded in two-dimensional space the elementary configurations are two. In fact, decreasing the scale of a box by a factor two, each occupied box is divided in two sub-boxes: the type-one configuration consists of one occupied sub-box and an empty one, and the type-two configuration has both sub-boxes occupied. The probabilities of occurence in the process of fine graining of these configurations are indicated by C_1 and C_2 respectively. The average number of occupied sub-boxes appearing at each level of fine graining from one occupied box is given by

$$\langle n \rangle = \sum_i n_i C_i = C_1 + 2C_2 \tag{1}$$

where n_i is the number of occupied sub-boxes in the corresponding configuration. The fractal dimension of the aggregate can be directly related to $\langle n \rangle$ by the relation:

$$D = 1 + \frac{\ln\langle n \rangle}{\ln 2}. \tag{2}$$

The problem is to define the asymptotic distribution of the C_i. In this respect we have to define an appropriate iterative transformation and study its fixed point. The FST can be thought of as an equation of motion for $\langle n \rangle$ in the 'growth' direction 'y', that is, the rate of change of the C_i in this direction. Using the translational invariance of the fractal properties of the structure as revealed by fine graining, we search for the fixed point ($\mathrm{d}\langle n \rangle/\mathrm{d}y = 0$) of the equation of motion. The FST matrix elements ($M_{i,j}$) are the conditional probabilities that link the distributions C_1 and C_2 of an intersection set to the next ones in the growth direction. The renormalization group would be based on the property of invariance with respect to a change of scale, whereas the fixed-scale transformation is based on the property of invariance with respect to the dynamical evolution at the same scale. The fixed point equation is

$$\begin{pmatrix} C_1^{k+1} \\ C_2^{k+1} \end{pmatrix} = \begin{pmatrix} M_{1,1} & M_{1,2} \\ M_{2,1} & M_{2,2} \end{pmatrix} \begin{pmatrix} C_1^k \\ C_2^k \end{pmatrix}. \tag{3}$$

In order to define these matrix elements it is necessary to specify the boundary conditions. Different boundary conditions give rise to different values of the elements $M_{i,j}$. In this case the $M_{i,j}$ are defined as the average of matrix elements evaluated with different boundary conditions. In order to include the fluctuations of these boundary conditions it is necessary to know the probability $P(\lambda)$ [4] that the pair of sites corresponding to the initial configuration 'i' has a void of size λ as a neighbour. The averaged matrix element becomes

$$M_{i,j} = \sum_{\lambda} P(\lambda) M_{i,j}(\lambda) . \tag{4}$$

To compute the matrix elements $M_{i,j}$ we should consider all the graphs linking the occupied sites in the initial cell to the sites of the next cell in the 'growth' direction. In fractal growth phenomena the weight of each graph is 'history dependent', in the sense that it depends on the order in which growing bonds construct the graph. Instead, dealing with equilibrium phenomena, the matrix elements $M_{i,j}$ only depend on the configuration (number of occupied bonds). Therefore the matrix elements are evaluated with a purely geometric approach based on the equilibrium properties of the model considered, where each connected configuration is characterized by its equilibrium statistical weight. In the statistical description of these equilibrium critical phenomena we use the grand canonical formulation where polymers of the same number of monomers have equal weights [3,13]. The grand canonical partition function is given by

$$Z(k) = \sum_{N} \Omega_N k^N . \tag{5}$$

Here Ω_N denotes the number of different shapes of size N in a given lattice, and k is the analogue of the thermodynamic monomer fugacity. The weight Ω_N is different for SAW or LA. For SAW there is the constraint that each walk can not intersect itself, while for LA all connected clusters are considered. When k is equal to k_c there is no characteristic cluster size and we are at the critical point. Here we define as cluster the connected configurations of monomers. The average end-to-end distance, or the average gyration radius in the grand canonical formulation, diverges, for $k \to k_c^-$, as

$$\xi(k) \sim (k - k_c)^{-\nu} \tag{6}$$

where ν is a universal critical exponent. The analogy of the above relation to thermal phase transitions motivates the definition of ν as the polymer critical correlation length exponent. In the limit $k \to k_c^-$ we can also write

$$\langle N \rangle \sim \xi^{1/\nu} , \tag{7}$$

Since in a self-similar structure we can define the fractal dimension through the relation

$$\langle N \rangle \sim \xi^D \tag{8}$$

the exponent ν can be related to the fractal dimension of the critical cluster [14] by

$$D = \frac{1}{\nu} . \tag{9}$$

This relation makes clear the connection with the fractal nature of the problem.

3. Self-avoiding walk in two and three dimensions

A SAW on an infinite lattice is a walk starting at a seed site and continuing by taking successive steps in a randomly chosen direction but avoiding its past track. In order to study the critical behaviour of polymers by the FST we will use the relation (9) between the fractal dimension D and the critical exponent ν. We use the SAW grand canonical description defined in the preceding section and therefore the iterative scheme of the FST method has to be applied at the critical point, where the self-similarity is ensured. From a statistical point of view this implies $k = k_c$. In this way the critical fugacity, a well known quantity from numerical simulations, will be the external input to obtain the critical exponents from the FST theory. The two-dimensional SAW on a square lattice, given its simple topology, is the easiest model to be studied within the FST approach. The definition of the model allows identification of only one 'growing' point. In order to apply the FST we need to evaluate the conditional probability that starting from a configuration of type 'i', a configuration of type 'j' follows in the 'growth' direction. Following the scheme introduced in [4] we start with a configuration of type 'i'. Consider all the possible 'growth' configurations inside the column on top of the initial frozen cell that lead to a configuration of type 'j' (see figure 1). We have to ensure the infinite connectivity of the critical configuration [5], i.e. the starting configuration must be connected to a line at a certain distance, now corresponding to the order of the calculation. In figure 1, where a second-order calculation is shown, the line is the upper broken line at the distance of two lattice constants. We consider only the configurations inside the column because we are only interested in relative probabilities. However, this may become an over-simplification if we attempt very high-order calculations. The evaluation of the $M_{i,j}$ elements is simplified for SAW because the $M_{i,j}$ will be equal for all 'i' at fixed 'j'. In fact, at this level of approximation, there is just one 'growing' site and the boundary conditions for the 'growth' column are irrelevant because closed boundary conditions never appear. In the grand canonical formulation, each configuration has a statistical weight given by k_c to the power of the number of bonds in the configuration. From these weights we can compute the normalized probability of each growth configuration. For example in figure 1 we have a statistical weight k_c^2 for the first configuration and k_c^3 for the second one. It follows that the normalized conditional probabilities of the growing configurations are

$$M_{1,1} = \frac{k_c^2}{k_c^2 + k_c^3} \qquad M_{1,2} = \frac{k_c^3}{k_c^2 + k_c^3}\,. \tag{10}$$

By using the critical fugacity $k_c = 0.379$ [7] and (2), (3) and (9), we obtain

$$\nu^{(\text{II-order})} = 0.740\,. \tag{11}$$

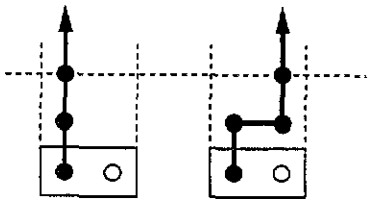

Figure 1. Second-order configurations for the two-dimensional SAW. The diagrams are connected up to the broken line corresponding to calculation order. We always use configurations identified by occupied bonds.

This result is already in excellent agreement with the exact value $\nu = 0.75$. Nevertheless we perform a third-order calculation to test the convergence of the method. In figure 2(a) the corresponding elementary 'growth' configurations are reported. The connectivity is now enforced up to the third line. Considering only growth within the column could be an over-simplification. Thus, we also take into account processes outside the column of growth that lead to the visitation by the SAW of a site within the column (figure 2(b)). These 'external' configurations are chosen by considering the configuration along the 'lateral border' (see figure 2(b)) of the column which are up to one order greater in k_c with respect to the internal configurations. Using these prescriptions the calculation becomes comparable to the open–closed FST scheme. Note that in the RSRG approach [15, 16] taking into account extra configurations would amount to enlarging the basic cell and to a higher computational complexity. On the other hand, in our scheme we can try to systematically test the influence of these contributions. Developing the calculation as outlined before we obtain for the matrix elements

$$M_{1,1} = \frac{k_c^3 + k_c^4 + k_c^5 + k_c^6}{k_c^3 + 2k_c^4 + 2k_c^5 + 2k_c^6} \tag{12}$$

$$M_{1,2} = \frac{k_c^4 + k_c^5 + k_c^6}{k_c^3 + 2k_c^4 + 2k_c^5 + 2k_c^6} \tag{13}$$

and from (2), (3) and (9) for the critical exponent

$$\nu^{(\text{III-order})} = 0.745\,. \tag{14}$$

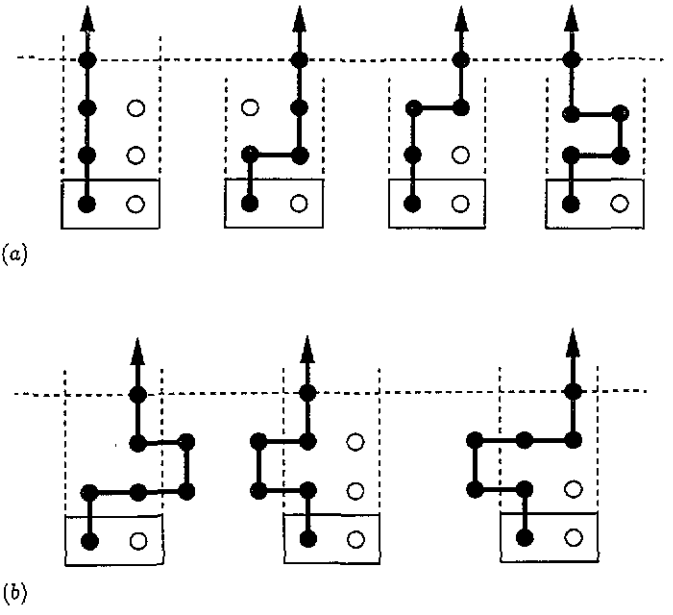

Figure 2. (a) Diagrams connected up to third order for the two-dimensional SAW. (b) New configurations corresponding to the relevant processes outside the growth column. It is worth remarking that the statistical weights of these external configurations are comparable with those of internal configurations. This is not the case in the second-order calculation.

We have also developed the fourth-order calculation, for which we report only the final result:

$$\nu^{(\text{IV-order})} = 0.746. \tag{15}$$

These results confirm the convergence of the method and its accuracy in evaluating the critical exponent. The relative simplicity of this model allows an important check of the whole FST method. In section 2 we have seen that the FST scheme of calculation depends on the choice of the elementary configurations considered. Instead of the two-site starting cell, corresponding to the simplest generators, let us consider a three-site starting cell. The FST results clearly should depend as little as possible upon this choice. By using a three-box fragmentation scheme, the number of elementary configurations becomes five. In type-one and -two only one site in the central and lateral position, respectively, are occupied. In type-three and -four occupations and vacancies are reversed. In type-five all the sites are occupied. The $M_{i,j}$ matrix is now a 5×5 matrix. In the SAW application this matrix has only five different elements ($M_{i,j} = M_{1,j}, \forall i, j$). Performing the calculations as before we found, at third order, $\nu = 0.742$. This result is practically the same as the one obtained with two elementary cells and confirms the independence of the FST from the choice of cell to which the elementary configurations refer. It is straightforward to generalize the approach of the previous section to the case of the three-dimensional self-avoiding walk [1–3]. The model is defined on a cubic lattice in which the walker can randomly move. This model mimics the statistical behaviour of a polymer embedded in three dimensional space. Here too we have a critical step fugacity, in the grand canonical formulation, at which the self-similarity of the walk is ensured. Now, the intersection of the structure with a plane is considered and the box covering is done with squares of edge L. During the fine graining we further subdivide each of these boxes into four sub-boxes of edge $L/2$. The possible resulting configurations are five, each one with the corresponding multiplicity due to non-equivalent rotations [17]. The average number of occupied sub-boxes generated in the fine graining process is

$$\langle n \rangle = 4C_5 + 3C_4 + 2C_3 + 2C_2 + C_1. \tag{16}$$

The fractal dimension is then given by the relation (5). Here the property of the SAW of having only one growing site leads to a great simplification in the calculation. The evaluation of the matrix elements is done along the lines of the two-dimensional calculation. In the 3D case we have to look at all the configurations in the 3D column above the starting 2×2 frozen basic configurations of four sites. Here too we must ensure the connectivity appropriate to the chosen order. We report in figure 3 an example of configurations contained in the 'growth' column. Up to the second and third order of calculation we find, using $k_c = 0.2135$ [9],

$$\nu^{(\text{II-order})} = 0.655 \tag{17}$$

$$\nu^{(\text{III-order})} = 0.632. \tag{18}$$

In the third-order calculation we did not consider walk configurations external to the growth column. These configurations, in the 3D case, are not longer negligible. In fact, due to the higher coordination number of the lattice, we have a great number of external walks with weights comparable to that of the internal ones. Including these configurations the final result is

$$\nu^{(\text{III-order})} = 0.593. \tag{19}$$

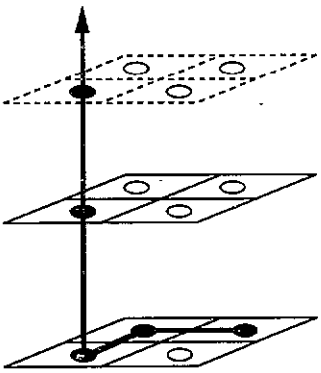

Figure 3. One example of configuration for the three-dimensional SAW. Here the diagrams must be connected to a plane at a distance corresponding to the order of calculation.

The great improvement of agreement (1%) with the numerical value of $\nu = 0.588$ [9] is mainly due to the fact that most of the external contributions increase the global statistical weight of the conditional probabilities $M_{i,1}$ and $M_{i,2}$. The fractal dimension rises up and the critical exponent ν decreases. So, also in this case, we can evaluate the contribution due to external configurations and improve the convergence towards the expected result. Moreover the appreciable contribution of these external configurations gives an indirect but clear indication of why real space renormalization group calculations do not show convergence for the 3D SAW unless very large cells are used.

4. Branched polymers

Branched polymers have the same critical properties as lattice animals. The scheme of calculation for LA is quite different from that for the SAW. In this case the configurations may branch, may have loops and the growing site may not be unique. This complication leads to the need of introducing the fluctuations of the boundary conditions and of setting up the full scheme of the FST framework. Using open boundary conditions we have to consider at second order, the configurations depicted in figure 4. Following the lines of the previous section we have to use k_c= 0.191 [6] for the critical step fugacity and to enforce connectivity in order to be at the critical point. We use the critical step fugacity of LA with loops and for this reason we consider also the looped diagrams in the evaluation of the matrix elements. On the contrary, the use of k_c relative to LA without loops should correspond to the elimination of the closed loop configurations in the calculation. It is worth remarking that in the LA case starting with different configurations leads to different matrix elements. The normalized conditional probability for growth configurations are, at second order,

$$M_{1,2}^{\mathrm{op}} = \frac{2k_c^3 + k_c^4}{k_c^2 + 2k_c^3 + k_c^4} \tag{20}$$

$$M_{2,1}^{\mathrm{op}} = \frac{2k_c^3}{2k_c^3 + 8k_c^4 + 6k_c^5 + k_c^6} \tag{21}$$

where the superscript 'op' means 'open boundary conditions'. Using (3) we obtain the critical exponent:

$$\nu^{\mathrm{op}}(\mathrm{II}) = 0.690\,. \tag{22}$$

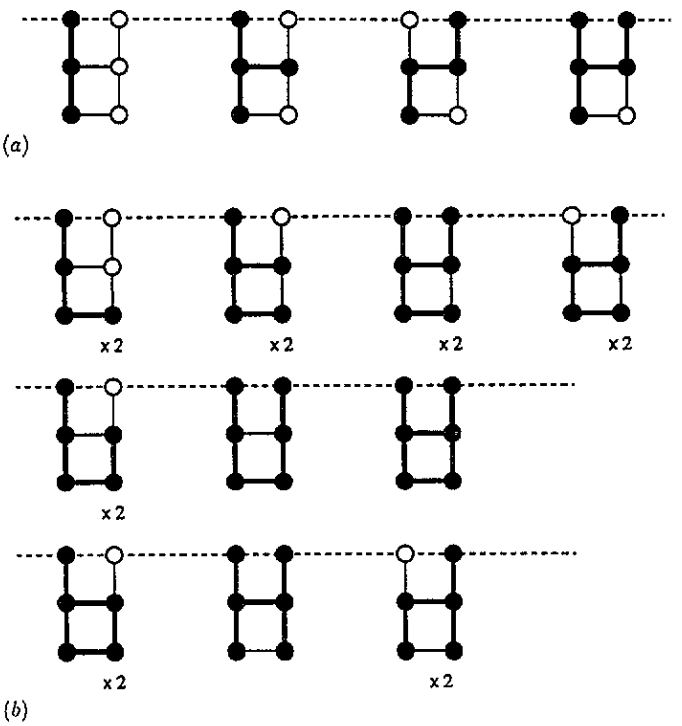

Figure 4. Second-order connected diagrams necessary for the evaluation of the matrix element in the case of branched polymers. (*a*) Configurations starting from a cell of type one. (*b*) Configurations starting from a cell of type two.

We can then perform a third-order calculation enforcing the connectivity up to three lattice constants obtaining

$$\nu^{\mathrm{op}}(\mathrm{III}) = 0.672\,. \tag{23}$$

We can turn now to the analysis of closed boundary conditions [4]. Closed configurations correspond to having an extra occupied site on the right of the starting configuration. In order to understand the effect of the closed boundary conditions we can consider the diagrams in figure 5. In this case one of the sites left empty may be occupied by a branch that originates from the occupied sites introduced by the boundary condition. The configurations are now the sum of those used in the open boundary conditions calculation plus those originated by the lateral bond weighted by an extra k factor. In addition there are some configurations which did not appear previously where the connectivity is ensured through the boundary conditions (see figure 5). These effects were clearly absent in the SAW diagrams. In figure 5 are drawn some of the new diagrams present in the closed boundary condition scheme of calculation. In the 'open–closed' approximation [4] the iterative transformation becomes nonlinear in C_1 and C_2, but again one can write the explicit solution for the fixed point:

$$C_1 = \left(M^{\mathrm{cl}}_{1,2} + 2M^{\mathrm{cl}}_{2,1} - \tfrac{3}{2}M^{\mathrm{op}}_{2,1} - \left((\tfrac{3}{2}M^{\mathrm{op}}_{2,1} - M^{\mathrm{cl}}_{1,2} - 2M^{\mathrm{cl}}_{2,1})^2 - 4M^{\mathrm{cl}}_{2,1}A\right)^{1/2}\right)/2A \tag{24}$$

$$A = M^{\mathrm{cl}}_{1,2} + M^{\mathrm{cl}}_{2,1} - \tfrac{3}{2}(M^{\mathrm{op}}_{1,2} + M^{\mathrm{op}}_{2,1})\,. \tag{25}$$

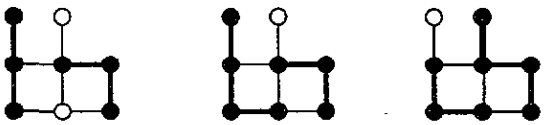

Figure 5. Configurations corresponding to closed boundary conditions. In this case one of the sites may be occupied by a branch introduced by the boundary conditions.

Using these equations we obtain

$$\nu^{\text{op-cl}}(\text{II}) = 0.664 \tag{26}$$

$$\nu^{\text{op-cl}}(\text{III}) = 0.644 \tag{27}$$

which is in excellent agreement with the numerical result $\nu = 0.641$ [6]. Also in this case the inclusion of external paths, via the fluctuations of boundary conditions, gives the most accurate estimate of the critical exponent.

Table 1. Radius exponent of two- and three-dimensional SAW and lattice animals computed with the FST method. The values reported correspond to increasing order of calculation and to the introduction of schemes for the inclusion of boundary conditions. Note that the boundary conditions treatment refers to the inclusion of the external configurations in the SAW models and to the complete open–closed FST scheme for the LA. The values obtained are compared with the exact or numerical results [6–9].

FST Scheme of calculation	SAW 2D	SAW 3D	Lattice animals
II-order	0.740	0.655	0.690
III-order	—	0.632	0.672
III-order (boundary-conditions treatment)	*0.745*	*0.593*	*0.644*
IV-order (boundary-conditions treatment)	0.746	—	—
Experimental results	0.75 (exact)	0.588	0.641

5. Summary and discussion

The problem of the critical behaviour of linear and branched polymers has been investigated with a great variety of theoretical and numerical methods. In table 1 the results of our FST approach are summarized and compared with the best existing estimates. As one can see from this table the agreement is very satisfactory. The application of the FST method to these problems is not only an important test for the approach itself but also highlights the difference between this method and the RSRG. In fact, the FST is quite different from RSRG not only because it works at a fixed scale, but also because the critical exponents are related directly to the fixed point parameters of the models instead of their derivative with respect to the relevant critical parameter. The basic new step is therefore that the FST method allows one to go directly from the non-universal critical parameter to the universal critical exponent. For this reason, in equilibrium statistical problems the FST needs the critical parameter as an external input. However, this quantity can be calculated by standard methods or even

by numerical simulations. On the other hand, given the critical parameter, the FST uses a fixed number of basic configurations (no proliferation) and allows one to take into account degrees of freedom external to the growing cell (in our case the external configurations) in a systematic way at a very low computational cost. The inclusion of growth processes outside the considered column up to the desired order and fluctuations of the boundary conditions are particularly relevant in the treatment of this type of problems and gives great accuracy in the numerical estimates. The simplicity and richness of the models used in this paper to describe polymers allowed us to stress and clarify all these essential points of the FST method and to focus on its basic differences from the theoretical approaches based on renormalization group ideas.

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