PHYSICAL REVIEW A VOLUME 42, NUMBER 10 15 NOVEMBER 1990

Entropy of flexible chains placed on Bethe and Husimi lattices

Jürgen F. Stilck* and Mario J. de Oliveira
Instituto de Física, Universidade de São Paulo, Caixa Postal 20 516, 01 498 São Paulo, São Paulo, Brazil

(Received 19 March 1990)

We consider the problem of placing self- and mutually avoiding chains, each formed by M consecutive monomers, on the Cayley and Husimi trees. As particular cases, we could mention the dimer ($M=2$) and the polymer ($M\rightarrow\infty$) problems. Defining an activity x for a monomer, we obtain the density $\rho(x)$ of sites occupied by chains in the central region of the trees, as well as the entropy as a function of ρ. On the Bethe lattice (central region of the Cayley tree), we were able to obtain closed expressions for general M. On the Husimi lattice (central region of the Husimi tree), only for the case of dimers were closed expressions found, and the other cases were treated numerically.

I. INTRODUCTION

The problem we want to address is the calculation of the entropy of self- and mutually avoiding chains placed on a lattice. The chains are supposed to be flexible, which means that no energy is paid to bend a chain. Also, besides the infinite excluded-volume interaction, we are assuming no interactions between the chains, so that the problem we are considering is athermal. Nevertheless, it is worth mentioning that the methods we use may be easily applied in cases where bending energies and other short-range interactions have to be taken into account. We are faced, therefore, with a combinatorial problem on a lattice, and we consider the general case where a given fraction ρ of the lattice sites are occupied by monomers belonging to the chains, whose length (number of monomers or molecular weight) will be denoted by M.

When each chain is formed by just two monomers ($M=2$), we have the dimer problem,[1] and for the particular case where all lattice sites are occupied by dimers ($\rho=1$), the exact solution of the problem is known on the square lattice.[2] Another particular case which was already considered extensively in the literature is the polymer problem ($M\rightarrow\infty$),[3] and when $\rho=1$ (Hamilton walks) an exact solution is known on two-dimensional Manhattan lattices.[4]

Subsets of the general problem have been investigated by a variety of techniques such as mean-field and Bethe approximations,[5] exact calculations,[6] series expansions,[7,8] transfer-matrix methods,[9] and field-theoretic approaches.[10] Recently, on hypercubic lattices, an exact field-theoretic representation of the problem was found, and the entropy was evaluated up to order z^{-2}, where z is the coordination number of the lattice.[11] Thus corrections are found to the mean-field results (which are of the Flory type and are exact in the infinite coordination limit $z\rightarrow\infty$).

In this paper we obtain the exact solution of the general problem on two structures. The first of these structures is often referred to as the Cayley tree. The thermodynamic properties of models defined on the Cayley tree are strongly influenced by its pathologically large surface. The solution we obtain is for the deep interior of the Cayley tree, which is called the Bethe lattice.[12] The second structure we consider is the Husimi tree.[13] Again our solution is for the deep interior of this tree, which we will call the Husimi lattice. These results may be considered as closed form approximations to the solution on hypercubic lattices. It should be remarked that for finite chains no phase transition should be observed in the problem we are considering, since it may be looked at as a noninteracting lattice gas. Only in the polymer limit $M\rightarrow\infty$ is a nonanalyticity expected to be present in the thermodynamic functions associated to the model.

In Sec. II we define the problem more precisely, and in Sec. III the results on the Bethe lattice are obtained. The solution of the model on the Husimi tree may be found in Sec. IV. Results are presented and discussed in Sec. V and finally a summary of the conclusions is given in Sec. VI.

II. MATHEMATICAL FORMULATION OF THE PROBLEM

Let $W_N(m)$ be the number of ways to place p chains, each occupying M neighboring lattice sites, on a lattice of N sites, with $m=Mp$. The density ρ of sites occupied by monomers belonging to chains will be $\rho=m/N$. In the thermodynamic limit $N\rightarrow\infty$, with ρ held fixed, the entropy per lattice site is given by

$$s(\rho)=\lim_{N\rightarrow\infty} N^{-1}\ln[W_N(m)] \ . \tag{1}$$

For the purpose of our calculations, it is convenient to work in the grand-canonical ensemble, so the number of chains placed on the lattice will not be held fixed. The grand-canonical partition function $Y_N(x)$ will be given by

$$Y_N(x)=\sum_{m=0}^{N} x^m W_N(m) \ , \tag{2}$$

where x is the activity of one monomer belonging to a chain. The activity of a chain will be x^M. The summation on m is over the multiples of M.

In this new ensemble the density $\rho(x)$ will be given by

$$\rho(x)=x\frac{d}{dx}[\phi(x)] , \tag{3}$$

where

$$\phi(x)=\lim_{N\to\infty} N^{-1}\ln Y_N(x) . \tag{4}$$

In the thermodynamic limit $s(\rho)$ and $\phi(x)$ will be related to each other through the following Legendre transformation:

$$\phi(x)=\max_{\rho}[s(\rho)+\rho\ln(x)] \tag{5}$$

from which it follows that

$$\frac{d}{d\rho}[s(\rho)]=-\ln(x) . \tag{6}$$

So, if $x(\rho)$ is known, the entropy may be calculated by performing the integration

$$s(\rho)=-\int_0^{\rho}[\ln(x)]d\rho' . \tag{7}$$

Another quantity that is often used in connection with the combinatorial problem of flexible chains on a lattice[9] is the connectivity constant $\mu(\rho)$, which is related to the asymptotic behavior of the number of configurations, that is,

$$W_N\sim\frac{\mu^{pM}}{p!} \tag{8}$$

for large N. For finite values of M, however, μ diverges in the thermodynamic limit as $N^{1/M}$. It is, therefore, convenient to introduce the quantity $\omega(\rho)$ defined as

$$\mu(\rho)=\omega(\rho)N^{1/M} . \tag{9}$$

For the case of polymers ($M\to\infty$), we have $\mu(\rho)=\omega(\rho)$.

In this work, however, we will not concentrate our attention on $\omega(\rho)$ since it may be calculated from the entropy. Actually, we have

$$\omega(\rho)=\left[\frac{\rho}{Me}\right]^{1/M}\exp\left[\frac{s(\rho)}{\rho}\right] , \tag{10}$$

so, for brevity, only the entropy will be calculated below.

III. SOLUTION OF THE BETHE LATTICE

We now calculate the partition function for chains placed on a Cayley tree with an arbitrary coordination z. In a procedure closely related to the solution of the Ising model presented by Baxter[12] we define M partial partition functions on rooted sub trees (see Fig. 1), labeling them according to the configuration of their root site. Thus g_1 is the partial partition function of a sub tree with no chain incident on the root site from above, and g_i, for $2\le i\le M$, refers to a sub tree with the ith monomer of a chain located on the root site. The definition of the partial partition functions is illustrated in Fig. 2.

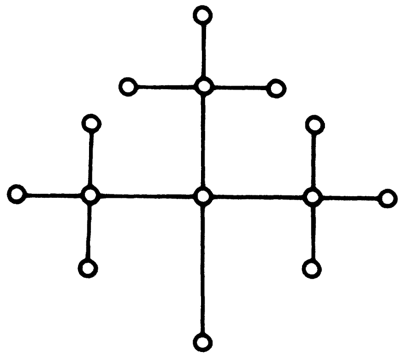

FIG. 1. A sub tree of a Cayley tree. The drawing is for $z=4$ ($r=3$).

It is straightforward to write down recursion relations between partial partition functions g_i of sub trees with a certain number of generations and those g_i' of sub trees with on additional generation. This is done considering the operation of attaching $r=z-1$ sub trees to a new root site. The result is

$$g_1'=g_1^r+rxg_Mg_1^{r-1}+\frac{r(r-1)}{2}xg_1^{r-2}\sum_{j=2}^{M-1}g_jg_{M-j+1} , \tag{11a}$$

$$g_2'=xg_1^r , \tag{11b}$$

$$g_k'=rxg_1^{r-1}g_{k-1},\quad 3\le K\le M . \tag{11c}$$

In the expression for g_1' we remark that the first term corresponds to having all r sub trees attached to the new root site with empty root sites, the second term corresponds to the situation where a chain end point is located on one of the root sites of the r sub trees, and in the last term a chain has one of the internal monomers on the site close to the new root site.

Now, it is convenient to define new variables $R_j\equiv g_{j+1}/g_1$, $j=1,2,\ldots,M-1$, and the recursion relations for them will be

$$R_1'=\frac{x}{D} , \tag{12a}$$

$$R_j'=\frac{rx}{D}R_{j-1},\quad j=2,3,\ldots,M-1 \tag{12b}$$

where

$$D=1+rxR_{M-1}+\frac{r(r-1)}{2}x\sum_{j=2}^{M-1}R_{j-1}R_{M-j} . \tag{13}$$

Any density in the central region of the Cayley tree [in

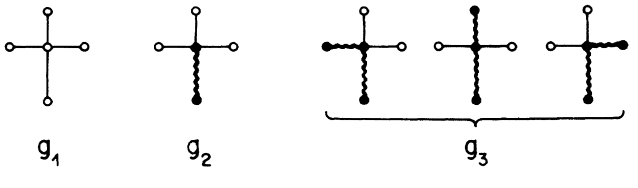

FIG. 2. Root configurations of sub trees on a Cayley tree for $z=4$.

particular, $\rho(x)$, which is needed for the calculation of the entropy] may be written as a function of the R's and since we are interested in results for an infinite lattice, the fixed point values R_i^* of R_i should be considered, since they are attained after an infinite number of iterations of the recursion relations. The fixed point values R_i^* have a quite simple structure: $rR_1^* = R_j^*/R_{j-1}^*$, $j=2,3,\ldots,M-1$. If we introduce an auxiliary variable α by $\alpha = rR_1^*$, we have $R_j^* = \alpha^j/r$. From Eqs. (12a) and (13) we obtain the following equation for α:

$$rx = \alpha + x\alpha^M \left[1 + \frac{r-1}{2r}(M-2) \right] . \tag{14}$$

After solving this equation for α, we obtain R_1^*, $R_2^*, \ldots, R_{M-1}^*$.

The partition function of the model on the Cayley tree is obtained by the operation of connecting z sub trees to the central site. The result is

$$Y = g_1^{r+1} + (r+1)xg_1^r g_M + \frac{r(r+1)}{2} x g_1^{r-1} \sum_{j=2}^{M-1} g_j g_{M-j+1} \tag{15}$$

and, again, the first term corresponds to not having a monomer on the central site, whereas in the two other terms there is a monomer on the central site. If we were interested in the thermodynamic properties of the model on the full Cayley tree, they could be obtained through the thermodynamic potential associated to the partition function (15). Since it is the behavior of the model in the deep interior of the tree we are interested in (Bethe lattice), we write down an expression for the density of monomers at the central site

$$\rho = \frac{1}{Y} \left[(r+1)xg_1^r g_M + \frac{r(r+1)}{2} x g_1^{r-1} \sum_{j=2}^{M-1} g_j g_{M-j+1} \right] . \tag{16}$$

In the thermodynamic limit, this expression may be written in terms of α. We get

$$\rho = \frac{\beta}{1+\beta} \quad \text{where } \beta = \frac{r+1}{2r} x M \alpha^{M-1} . \tag{17}$$

If α is obtained as a function of x, then we get ρ as a function of x. However, it is easier to take the opposite approach and obtain x as a function of ρ. From Eq. (14) we have the expression

$$x = \frac{2r\alpha}{2r^2 - [2+(r-1)M]\alpha^M} . \tag{18}$$

Now, if we eliminate x from Eqs. (17) and (18) we obtain

$$\alpha = \left[\frac{2r^2\rho}{zM - 2(M-1)\rho} \right]^{1/M} . \tag{19}$$

Equations (18) and (19) give, then, x as a function of ρ. After some algebra, we have

$$x = x_{\mathrm{MF}} \left(\frac{z-1}{z} \right)^{2/M-1} \left[1 - \frac{2}{z} \left(1 - \frac{1}{M} \right) \rho \right]^{1-1/M} \tag{20}$$

where

$$x_{\mathrm{MF}} = \frac{1}{z(1-\rho)} \left[\frac{2z}{M} \rho \right]^{1/M} \tag{21}$$

is the expression for x in the limit of infinite coordination number, which corresponds to the mean-field result.

It is not difficult to perform the integration in Eq. (7) with the expression (20) for $x(\rho)$. The following expression for the entropy per site is obtained:

$$s(\rho) = s_{\mathrm{MF}}(\rho) + \left(1 - \frac{2}{M} \right) \rho \ln \left(1 - \frac{1}{z} \right) + \left(1 - \frac{1}{M} \right) \rho + \left[\frac{z}{2} - \left(1 - \frac{1}{M} \right) \rho \right] \ln \left[1 - \frac{2}{z} \left(1 - \frac{1}{M} \right) \rho \right] \tag{22}$$

where

$$s_{\mathrm{MF}}(\rho) = -(1-\rho)\ln(1-\rho) - \frac{\rho}{M} \ln \frac{2\rho}{M} + \left(1 - \frac{1}{M} \right) \rho (\ln z - 1) \tag{23}$$

is the mean-field result for the entropy.

It is of some interest to verify how the closed form (22)–(23) for the entropy on the Bethe lattice, which may be considered to be an approximation for the entropy on a regular Bravais lattice with coordination number z, compares with the expansion of the entropy in powers of $1/z$ for hypercubic lattices.[11] The expansion of the correction to the mean-field entropy in (22) up to second order in $1/z$ gives

$$s = s_{\mathrm{MF}} + \left[-\left(1 - \frac{2}{M} \right) \rho + \left(1 - \frac{1}{M} \right) \rho^2 \right] \left(\frac{1}{z} \right) + \left[-\frac{1}{2} \left(1 - \frac{2}{M} \right) \rho + \frac{2}{3} \left(1 - \frac{1}{M} \right)^3 \rho^3 \right] \left(\frac{1}{z} \right)^2 . \tag{24}$$

Comparing this expression with the expansion in powers of $1/z$ by Nemirovsky and Coutinho-Filho,[11] we see that the Bethe lattice solution is correct up to order $1/z$.

A particular case which is worth looking at is the polymer limit $M \to \infty$. From Eq. (14) for α, it is apparent that, in this limit, two situations should be considered. If $rx \leq 1$, we have $\alpha = rx$ and $M\alpha^M = 0$ when $M \to \infty$. Thus, from Eq. (17), we see that $\rho = 0$. Now, when $rx > 1$, it follows that $\alpha = 1$ and $M\alpha^M = 2r(rx-1)/(rx-x)$, when $M \to \infty$. So, in this case we get a nonzero limit for ρ, namely,

$$\rho = \frac{(r+1)(rx-1)}{(r-1)+(r+1)(rx-1)} , \tag{25}$$

which is the result already obtained in a direct calculation of polymerization on the Bethe lattice, where a phase transition is present at $x_c = 1/r$.[14]

As expected, for any finite value of M, $\rho(x)$ is a continuous function, but in the polymer limit it will not be analytic at the transition activity x_c. The entropy (22) in the polymer limit $M \to \infty$ is given by

$$s(\rho)=\rho\ln(z-1)+\left[\frac{z}{2}-\rho\right]\ln\left[1-\frac{2}{z}\rho\right]-(1-\rho)\ln(1-\rho)\ , \tag{26}$$

and is consistent with the calculation by Nagle on the Bethe lattice for $\rho=1$.[6]

Another interesting particular case is the entropy of dimers ($M=2$). In this case, expression (22) gives

$$s(\rho)=-(1-\rho)\ln(1-\rho)-\frac{\rho}{2}\ln\rho z+\frac{z}{2}\left[1-\frac{\rho}{z}\right]\ln\left[1-\frac{\rho}{z}\right] \tag{27}$$

and again this result agrees with earlier work by Nagle.[7]

IV. SOLUTION OF THE HUSIMI LATTICE

As is well known, the Bethe lattice solution of a model, viewed as an approximation of this model on a Bravais lattice, takes into account only the coordination number of the lattice. As an example, no distinction is made, in this approximation, between the simple cubic and triangular lattices, since both have coordination numbers $z=6$. One way to improve this approximation is to define the model on a Husimi tree,[13] which is a tree built by putting together polygons attached to each other by their vertices. Therefore, on a Husimi tree, there are closed cycles, but they are all of the same size. As was argued in the Introduction, we will consider the properties of the model in the deep interior of the tree, the Husimi lattice. So, if we were interested in finding an approximation of a model on the triangular lattice, we could solve this model on a Husimi lattice with three triangles incident on each vertex similar to the one shown in Fig. 3. An exact solution on the Husimi lattice with three squares incident on each vertex would be an appropriate approximation for the solution of a model on a cubic lattice.

In this section we present a calculation of the entropy of chains of length M on a Husimi lattice built with squares. Since the elementary closed cycles on all hypercubic lattices are squares, our calculation may be viewed as an approximation of the problem on hypercubic lattices.

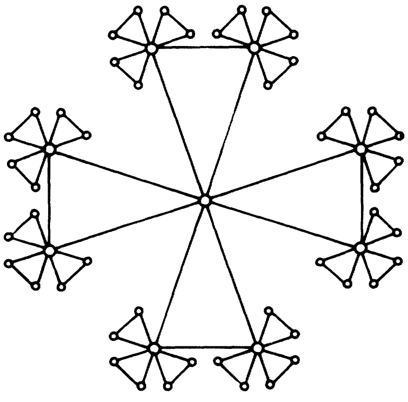

FIG. 3. Husimi tree formed with triangles with coordination number $z=8$.

A. Dimers

Let us consider a Husimi tree with $\sigma+1$ squares incident on each vertex, so that the coordination number will be $z=2\sigma+2$. Again, we obtain recursion relations for partial partition functions of the model on rooted sub trees. A sub tree with an additional generation is obtained by attaching three groups of σ sub trees to the vertices of a new root square. The fourth vertex of this root square will be the new root site as shown in Fig. 4. The labeling of the partial partition functions will be as follows: g_1 is the function of a sub tree with no dimer incident on the root site from above, and g_2 is the function of a sub tree with a dimer incident on the root site from above.

It is not difficult to obtain recursion relations for the partial partition functions g_1 and g_2. The result is

$$g_1'=(g_1^\sigma+x\sigma g_2 g_1^{\sigma-1})^3+2x^2g_1^{3\sigma}+2x^3\sigma g_1^{3\sigma-1}g_2\ , \tag{28a}$$

$$g_2'=2[xg_1^\sigma(g_1^\sigma+x\sigma g_2 g_1^{\sigma-1})^2+x^3g_1^{3\sigma}]\ . \tag{28b}$$

Defining a new variable R by $R=x\sigma g_2/g_1$, we get the following recursion relation:

$$R'=\frac{2\sigma x^2[(1+R)^2+x^2]}{(1+R)^3+2x^2(1+R)}\ . \tag{29}$$

The fixed point equation is

$$2\sigma x^4+[2\sigma(1+R)^2-2R(1+R)]x^2-R(1+R)^3=0\ , \tag{30}$$

with the real solution for x^2

$$x^2=\frac{R(1+R)}{2\sigma}\left[1-\frac{\sigma(1+R)}{R}+\left[1+\frac{\sigma^2(1-R)^2}{R^2}\right]^{1/2}\right]\ . \tag{31}$$

Now, to obtain the Husimi lattice solution, we consider the operation of attaching $\sigma+1$ sub trees to the central site of the tree, we obtain the following expression for the density of monomers on this site:

$$\rho=\frac{1}{Y}x(\sigma+1)g_2g_1^\sigma\ , \tag{32}$$

where

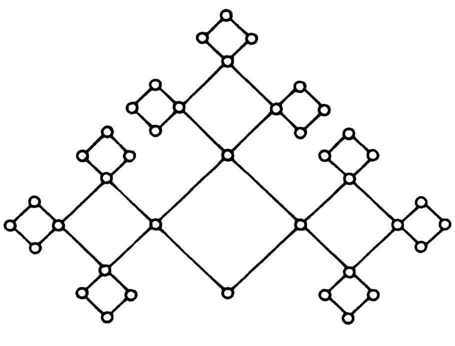

FIG. 4. A sub tree of a Husimi tree. The figure was drawn for $z=4$ ($\sigma=1$).

$$Y=g_1^{\sigma+1}+x(\sigma+1)g_2g_1^{\sigma} \ . \tag{33}$$

In the thermodynamic limit we get

$$\rho=\frac{(\sigma+1)R}{\sigma+(\sigma+1)R} \ . \tag{34}$$

Equations (31) and (34) give, then, x as a function of ρ:

$$x=x_{\mathrm{MF}}\left(1-\frac{2}{z}\rho\right)(1+A)^{1/2} \tag{35}$$

where

$$x_{\mathrm{MF}}=\left(\frac{\rho}{z}\right)^{1/2}\frac{1}{1-\rho} \tag{36}$$

is the mean-field result for dimers and

$$A=-\left(\frac{z}{2\rho}-1\right)+\left[\left(\frac{z}{2\rho}-1\right)^2+1\right]^{1/2} \ . \tag{37}$$

After performing the integration in Eq. (7) we get the following expression for the entropy:

$$s=s_{\mathrm{MF}}+\frac{1}{2}\left(\frac{z}{2}-\rho\right)\ln\left(1-\frac{2}{z}\rho\right)+\frac{\rho}{2}$$
$$+\frac{1}{2}\left(\frac{z}{2}-\rho\right)\ln(1+A)-\frac{z}{8}\ln(1+2A-A^2) \ , \tag{38}$$

where s_{MF} is the mean-field result given by

$$s_{\mathrm{MF}}=-(1-\rho)\ln(1-\rho)-\frac{\rho}{2}\ln\frac{\rho}{z}-\frac{\rho}{2} \ . \tag{39}$$

If the entropy (38) is expanded in powers of $1/z$ up to second order, the result is

$$s-s_{\mathrm{MF}}=\frac{\rho^2}{4}\left(\frac{1}{z}\right)+\frac{\rho^3}{12}\left(\frac{1}{z}\right)^2 , \tag{40}$$

and it is clear that these terms are the same as those of the Bethe lattice solution for $M=2$. Thus, the second-order term above is not correct for a Bravais lattice, although higher-order terms are improved when compared with those of the Bethe lattice solution.

B. Polymers

In the limit of infinite chains, it is possible to handle the problem on the Husimi tree by defining only three partial partition functions g_1, g_2, and g_3. They correspond to no chain incident on the root site from above, one chain, and two chains, respectively. The recursion relations for these functions are

$$g_1'=G_1^3+2G_1G_2+G_3 \ , \tag{41a}$$

$$g_2'=2\sigma x[g_1^{\sigma-1}g_2(G_1+G_2)+xg_1^{2\sigma-1}g_2G_1+x^2g_1^{3\sigma-1}g_2] \ , \tag{41b}$$

$$g_3'=\sigma^2x^2(g_1^{2\sigma-2}g_2^2G_1+2xg_1^{3\sigma-2}g_2^2) \tag{41c}$$

where

$$G_1=g_1^{\sigma}+\sigma xg_1^{\sigma-1}g_3+\frac{\sigma(\sigma-1)}{2}xg_1^{\sigma-2}g_2^2 \ , \tag{42a}$$

$$G_2=\sigma^2x^2g_1^{2\sigma-2}g_2^2 \ , \tag{42b}$$

$$G_3=\sigma^2x^3g_1^{3\sigma-2}g_2^2 \ . \tag{42c}$$

Defining the ratios $R_1=g_2/g_1$ and $R_2=g_3/g_1$, it follows that

$$R_1'=2\sigma R_1\frac{a^2+b+a+1}{a^3+2ab+b} \ , \tag{43a}$$

$$R_2'=\frac{b(a+2)}{a^3+2ab+b} \ , \tag{43b}$$

where

$$a=\frac{1}{x}+\sigma R_2+\frac{\sigma(\sigma-1)}{2}R_1^2 \ , \tag{44a}$$

$$b=\sigma^2R_1^2 \ . \tag{44b}$$

The density of monomers on the central site is given by

$$\rho=\frac{1}{Y}\left(x(\sigma+1)g_1^{\sigma}g_3+x\frac{\sigma(\sigma+1)}{2}g_1^{\sigma-1}g_2^2\right) , \tag{45}$$

where

$$Y=g_1^{\sigma+1}+x(\sigma+1)g_1^{\sigma}g_3+x\frac{\sigma(\sigma+1)}{2}g_1^{\sigma-1}g_2^2 \ . \tag{46}$$

In the thermodynamic limit we obtain

$$\rho=\frac{\beta}{1+\beta} \tag{47}$$

where

$$\beta=x(\sigma+1)R_2+x\frac{\sigma(\sigma+1)}{2}R_1^2 \ . \tag{48}$$

From the recursion relations we notice that there is always a nonpolymerized ($\rho=0$) fixed point $R_1=R_2=0$. This fixed point is stable whenever x is smaller than x_c, solution of

$$x_c^3+x_c^2+x_c=\frac{1}{2\sigma}=\frac{1}{z-2} \ . \tag{49}$$

So, the polymerization transition in the Husimi lattice occurs at a critical activity x_c given above.

C. Chains of Length M

In this section we present a calculation of the entropy of chains of length M ($M>2$ and finite) placed on the Husimi lattice. As before, g_1 will be the partial partition function of a sub tree with no chain incident on the root site from above, whereas g_i, with $2\le i<M$, is the function of a sub tree with the ith monomer of a chain on the root site. The partial partition function g_M comprises, besides root sites with the Mth monomer of a chain on it, also those configurations where two links of a chain are located on the bonds incident on the root site.

Again recursion relations may be obtained for the partial partition functions. The results are

$$g'_1 = A^3+2AB+C \ , \tag{50a}$$

$$g'_2 = 2xg_1^{\sigma}(A^2+B) \ , \tag{50b}$$

$$g'_3 = 2x[\sigma g_1^{\sigma-1}g_2(A^2+B)] \ , \tag{50c}$$

$$g'_4 = 2x[\sigma g_1^{\sigma-1}g_2(A^2+B)+x\sigma g_1^{2\sigma-1}g_2A+x^2g_1^{3\sigma}] \ , \tag{50d}$$

$$g'_i = 2x[\sigma g_1^{\sigma-1}g_{i-1}(A^2+B)+x\sigma g_1^{2\sigma-1}g_{i-2}A +x^2\sigma g_1^{3\sigma-1}g_{i-3}], \quad i=5,6,\dots,M-1 \tag{50e}$$

$$g'_i = 2x[\sigma g_1^{\sigma-1}g_{i-1}(A^2+B)+x\sigma g_1^{2\sigma-1}g_{i-2}A +x^2\sigma g_1^{3\sigma-1}g_{i-3}], \quad i=5,6,\dots,M-1$$

where

$$A = g_1^{\sigma}+x\sigma g_1^{\sigma-1}g_M+\frac{\sigma(\sigma-1)}{2}xg_1^{\sigma-2}\sum_{j=2}^{M-1}g_jg_{M-j+1} \ , \tag{51a}$$

$$B = x^2\left[\sigma^2g_1^{2\sigma-2}\sum_{j=2}^{M-2}g_jg_{M-j}+2\sigma g_1^{2\sigma-1}g_{M-1}\right] \ , \tag{51b}$$

$$C = x^2\left[\sigma^2g_1^{2\sigma-2}\sum_{j=2}^{M-3}g_jg_{M-j-1}+2\sigma g_1^{2\sigma-1}g_{M-2}\right] \ , \tag{51c}$$

$$D = 2x^3\left[\sigma^2g_1^{3\sigma-2}\sum_{j=2}^{M-4}g_jg_{M-j-2}+2\sigma g_1^{3\sigma-1}g_{M-3}\right] \ . \tag{51d}$$

Now, ratios of the partial partition functions may be defined as $R_i = g_{i+1}/g_1$. We have then

$$R'_1 = \frac{2(a^2+b)}{a^3+2ab+c} \ , \tag{52a}$$

$$R'_2 = \frac{2[\sigma R_1(a^2+b)+a]}{a^3+2ab+c} \ , \tag{52b}$$

$$R'_3 = \frac{2[\sigma R_2(a^2+b)+\sigma R_1a+1]}{a^3+2ab+c} \ , \tag{52c}$$

$$R'_1 = \frac{2[\sigma R_{i-1}(a^2+b)+\sigma R_{i-2}a+\sigma R_{i-3}]}{a^3+2ab+c} \tag{52d}$$

for $4 \le i \le M-2$, and

$$R'_{M-1} = \frac{2[\sigma R_{M-2}(a+b)^2+\sigma R_{M-3}a+\sigma R_{M-4}]+ac+d}{a^3+2ab+c} \tag{52e}$$

where

$$a = \frac{1}{x}+\sigma R_{M-1}+\frac{\sigma(\sigma-1)}{2}\sum_{j=2}^{M-1}R_{j-1}R_{M-j} \ , \tag{53a}$$

$$b = 2\sigma R_{M-2}+\sigma^2\sum_{j=2}^{M-2}R_{j-1}R_{M-j-1} \ , \tag{53b}$$

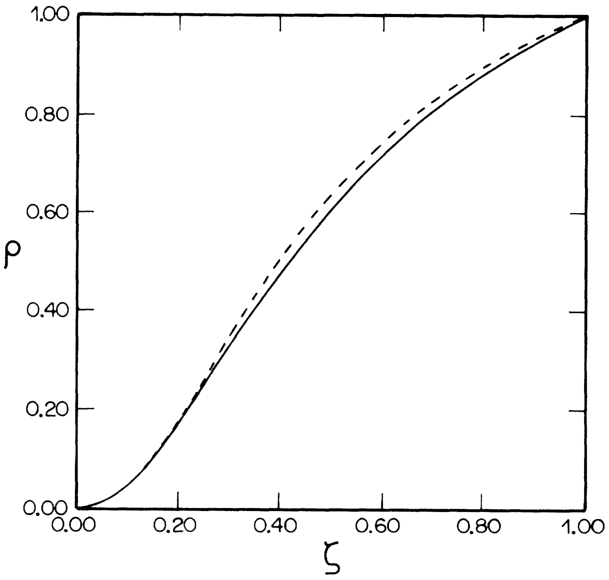

FIG. 5. Curves of the monomer density ρ as a function of $\zeta = x/(1+x)$ for dimers ($M=2$) placed on a lattice with coordination number $z=4$. Mean-field (solid) and Bethe lattice (dashed) results are shown.

$$c = 2\sigma R_{M-3}+\sigma^2\sum_{j=2}^{M-3}R_{j-1}R_{M-j-2} \ , \tag{53c}$$

$$d = 4\sigma R_{M-4}+2\sigma^2\sum_{m=2}^{M-4}R_{j-1}R_{M-j-3} \ . \tag{53d}$$

The partition function of the model on the complete Husimi tree is obtained connecting $\sigma+1$ sub trees to the central site. The result is

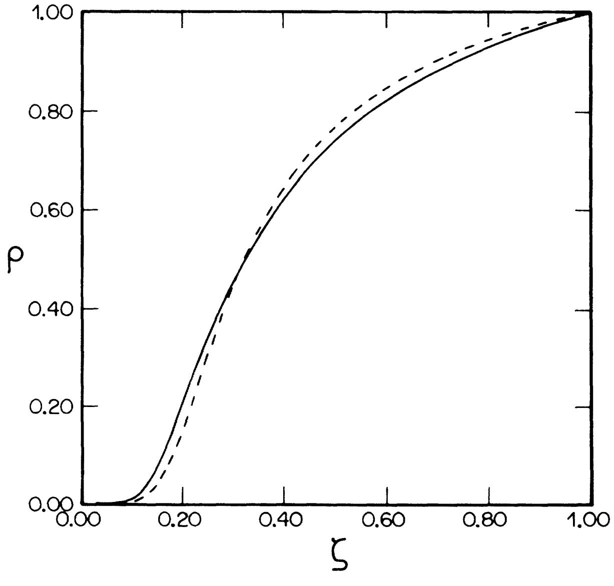

FIG. 6. Same as Fig. 5, for pentamers ($M=5$).

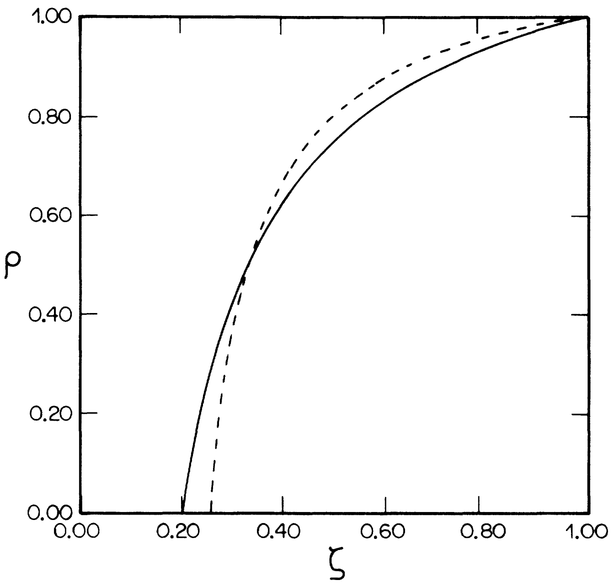

FIG. 7. Same as Fig. 5, for polymers ($M \rightarrow \infty$).

$$Y=g_1^{\sigma+1}+x(\sigma+1)g_1^{\sigma}g_M+x\frac{\sigma(\sigma+1)}{2}g_1^{\sigma-1}\sum_{j=2}^{M-1}g_jg_{M-j+1}\,, \tag{54}$$

and the density of monomers at the central site will be given by

$$\rho=\frac{\beta}{1+\beta}$$

$$\text{where } \beta=x(\sigma+1)\left[R_{M-1}+\frac{\sigma}{2}\sum_{j=2}^{M-1}R_{j-1}R_{M-j}\right]\,, \tag{55}$$

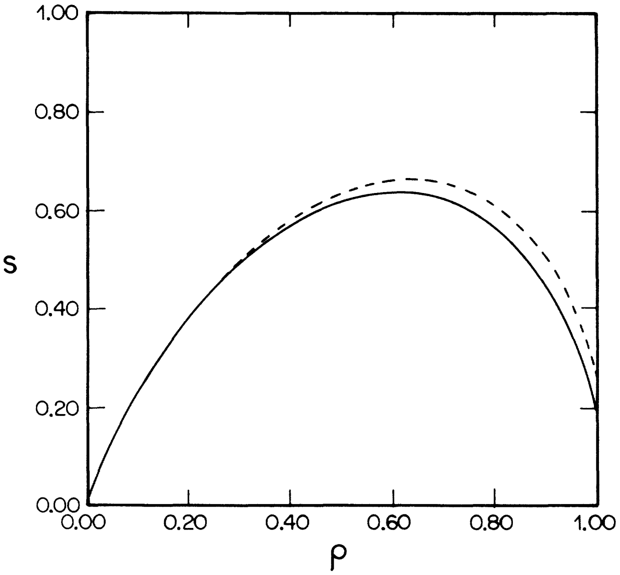

FIG. 8. Entropy as a function of the density ρ for dimers ($M=2$). Solid lines are mean-field and dashed lines are Bethe lattice results.

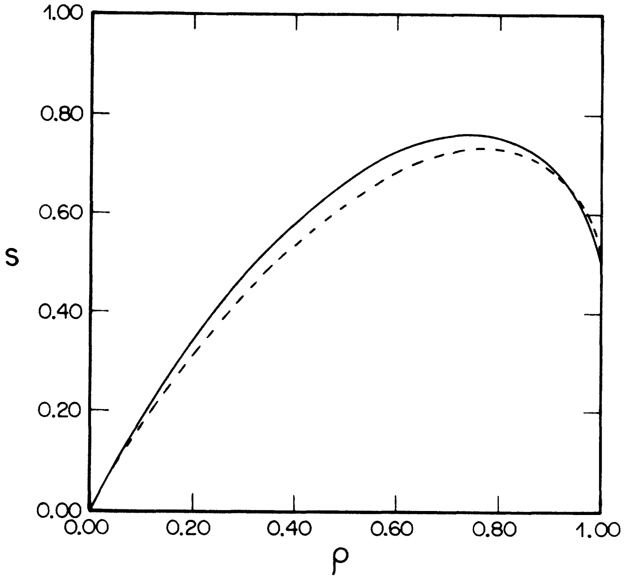

FIG. 9. Same as Fig. 8, for pentamers ($M=5$).

where, in the limit of an infinite tree, the fixed point values R_i^* should be employed.

Now the fixed point of the recursion relations (52) may be found numerically and, once the density ρ is calculated, the entropy follows by numerical evaluation of the integral in expression (7).

V. RESULTS

We present in Figs. 5–10 the plots of the monomer density ρ as a function of the "activity fraction" $\zeta \equiv x/(1+x)$ and of the entropy as a function of the density ρ, all for coordination number $z=4$. At the scale of

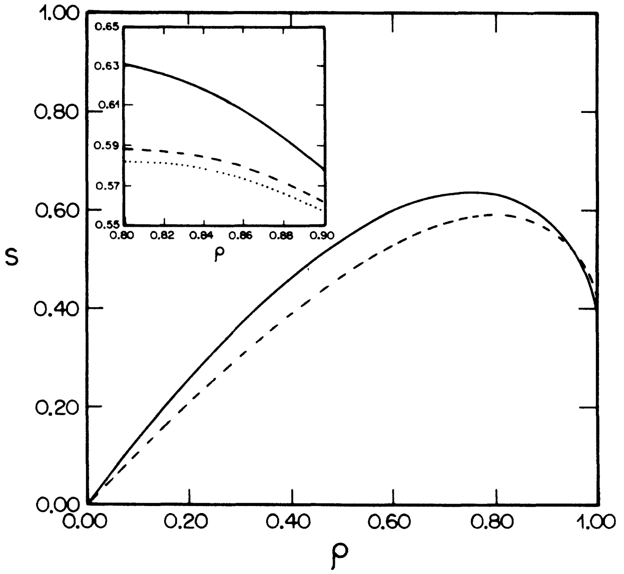

FIG. 10. Same as Fig. 8, for polymers ($M \rightarrow \infty$). In the inset, part of the graph is enlarged, and the result on the Husimi lattice is also plotted (dotted lines).

TABLE I. Entropy at full coverage ($\rho=1$) for square ($z=4$) and cubic ($z=6$) lattices in several approximations.

z	M	MF	Bethe	Husimi	First order	Second order	Best value
4	2	0.1931	0.2616	0.2674	0.2556	0.2687	0.2916[a]
4	5	0.4923	0.5067	0.5089	0.5023	0.5101	
4	∞	0.3863	0.4055	0.4090	0.3863	0.3967	0.3866[b]
6	2	0.3959	0.4401	0.4413	0.4375	0.4433	0.4465[c]
6	5	0.8167	0.8249	0.8255	0.8233	0.8268	
6	∞	0.7918	0.7985	0.7986	0.7918	0.7964	

[a] Reference 2.

[b] Reference 15.

[c] References 7 and 8.

the graphs, the results on the Husimi lattice are almost coincident with the ones obtained on the Bethe lattice, so only mean-field and Bethe lattice results are plotted. In the inset in Fig. 10 an enlarged portion of the graph is shown, and there the result on the Husimi lattice is also plotted. For larger values of z the differences between the three results are even smaller.

The curves corresponding to mean-field and Bethe lattice calculations came from the closed expressions obtained in Sec. III. For the case of the Husimi lattice the results were obtained numerically, except for dimers where we succeeded in obtaining a closed expression. One interesting feature that may be observed in Figs. 5, 6, and 7 is the development of the singularity in the function $\rho(x)$ as $M\rightarrow\infty$ (polymer limit). The graph for $M=5$ (Fig. 6) already shows curves $\rho(\zeta)$ which increase very slowly for small values of ζ (and, consequently, of x), and then the inclination of the curves grows considerably in a rather small interval of ζ. In the limit $M\rightarrow\infty$, the derivative of $\rho(\zeta)$ is discontinuous at $\zeta_c\equiv x_c/(1+x_c)$.

In Table I we present the results for the entropy of the chains in the limit $\rho=1$, corresponding to $z=4$ (square lattice) and $z=6$ (cubic lattice). In the case $M\rightarrow\infty$, this corresponds to the entropy of Hamilton walks. For comparison, we also show the results coming from the first- and second-order expansions in $(1/z)$,[11] and the best results known to us.

Finally, in Table II the critical activity of polymers on hypercubic lattices is given, for various values of z. It is apparent that at higher values of z the differences between results coming from different approximations become very small, as expected.

VI. CONCLUSION

We considered the problem of calculating the entropy of self- and mutually avoiding chains formed by M monomers placed on the Bethe lattice and on the Husimi lattice. It was convenient to formulate the problem in an ensemble which is grand canonical with respect to the number of monomers incorporated into chains. The activity of one monomer was denoted by x, and we calculated expressions of the density ρ of monomers on the lattice as a function of x. As expected, the functions $\rho(x)$ obtained are monotonic and analytic, with the exception of the polymer case $M\rightarrow\infty$, where a phase transition is observed at a critical activity x_c. The polymer density $\rho(x)$ is equal to zero for values of x smaller than x_c, and becomes nonzero for values of x larger than x_c.

In general, the solution of the problem on the lattices we considered is obtained through the evaluation of fixed points of a set of recursion relations. In the case of the Bethe lattice, it was possible to find an ansatz for this fixed point for general M, so we were able to find closed expressions for $\rho(x)$ and the entropy $s(\rho)$. The same happened for dimers on the Husimi tree. For chains with molecular weight larger than 2 on the Husimi tree we had to evaluate the fixed point numerically.

The solutions of the problem on cores of trees may be viewed as approximations to the exact solution on regular lattices. So, it is useful to compare the results with others already known. One comparison we made is with the exact expansion of the entropy in powers of $1/z$ for hypercubic lattices, obtained up to second order by Nemirovsky and Coutinho-Filho.[11] As expected, we found that if

TABLE II. Critical activity x_c for hypercubic lattices.

z	MF	Bethe	Husimi	First order	Second order	Best value
4	0.2500	0.3333	0.3425	0.3210	0.3526	0.3791[a]
6	0.1667	0.2000	0.2013	0.1969	0.2053	0.2135[b]
8	0.1250	0.1429	0.1432	0.1416	0.1450	0.1478[c]
10	0.1000	0.1111	0.1112	0.1105	0.1122	0.1132[c]

[a] Reference 16.

[b] Reference 17.

[c] Reference 18.

the Bethe lattice result for s is expanded in powers of $1/z$, the first term is coincident with the exact one. However, the second-order term of the entropy of dimers on the Husimi lattice is still wrong, although higher-order terms are improved relative to the Bethe lattice solution. We believe this situation to be the same for all molecular weights M.

In general, the Husimi lattice results are somewhat smaller than the value obtained from the second-order expansion in $1/z$. Nevertheless, in cases where exact or more precise values are available, the deviations of the Husimi lattice results are typically smaller than 1% for the case of the square lattice $z=4$. Since at $z \rightarrow \infty$ the mean-field approximation to this problem is exact, errors from all approximations become smaller as z is increased.

ACKNOWLEDGMENTS

This work was partially supported by Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq) and by Financiadora de Estudos e Projetos (FINEP), Brazil. We thank A. M. Nemirovsky and M. D. Coutinho-Filho for drawing our attention to the problem and for discussions.

---

[*] Present address: Departamento de Física, Universidade Federal de Santa Catarina, 88 049 Florianópolis, Santa Catarina, Brazil.

[1] J. F. Nagle, C. S. O. Yokoi, and S. M. Battacharjee, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1989), Vol. 13.

[2] H. N. V. Temperley and M. E. Fisher, Philos. Mag. **6**, 1061 (1961); M. E. Fisher, Phys. Rev. **124**, 1664 (1961); P. W. Kasteleyn, Physica **27**, 1209 (1961); J. F. Nagle, J. Math. Phys. **7**, 1484 (1966); **7**, 1492 (1966).

[3] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[4] P. W. Kasteleyn, Physica **29**, 1329 (1962).

[5] P. J. Flory, J. Chem. Phys. **9**, 660 (1941); **10**, 51 (1942); M. L. Huggins, *ibid.* **9**, 440 (1941); **10**, 151 (1942); Ann. N. Y. Acad. Sci. **44**, 431 (1943).

[6] J. F. Nagle, Proc. R. Soc. London, Ser. A **337**, 569 (1974).

[7] J. F. Nagle, Phys. Rev. **152**, 190 (1966).

[8] D. S. Gaunt, Phys. Rev. **179**, 174 (1969).

[9] B. Duplantier and H. Saleur, Nucl. Phys. B **290**, 291 (1987).

[10] H. Orland, C. Ikzykson, and C. de Dominicis, J. Phys. (Paris) Lett. **46**, L353 (1985).

[11] A. M. Nemirovsky and M. D. Coutinho-Filho, Phys. Rev. A **39**, 3120 (1989).

[12] R. Baxter, *Exactly Solved Models in Statistical Mechanics,* (Academic, London, 1982).

[13] K. Husimi, J. Chem. Phys. **18**, 682 (1950); T. Tsuchyia, Prog. Theor. Phys. **56**, 741 (1976).

[14] J. F. Stilck and J. C. Wheeler, J. Stat. Phys. **46**, 1 (1987).

[15] T. G. Schmaltz, G. E. Hite, and D. J. Klein, J. Phys. A **17**, 445 (1984).

[16] M. G. Watts, J. Phys. A **8**, 61 (1975).

[17] B. Derrida, J. Phys. A **14**, L5 (1981).

[18] M. E. Fisher and D. S. Gaunt, Phys. Rev. **133**, 224 (1964).