# Thermodynamic Behavior of Polymers on the Anisotropic Husimi Lattice

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We study a model for equilibrium polymerization on an anisotropic Husimi lattice of coordination number equal'to four, so that an additional energy E is associated with each bond of the polymer in a particular direction of the lattice. Two different polymerized phases are found in the phase diagram of the model, one of them having all lattice sites visited by the polymer. We compare our results with earlier Bethe lattice calculations on the same model.

## I. Introduction and definition of the model

Self- and mutually-avoiding chains placed on lattices have been used for quite a long time as models to study the properties of polymers[1]. Recently, a model for equilibrium polymerization[2] on an anisotropic lattice was solved on the Bethe lattice[3]. In this model, an additional energy E is associated with each polymer bond which is in a particular direction on the lattice. As an example, let us consider a square lattice. Each polymer bond may be oriented either in the horizontal or vertical direction, since it connects nearest-neighbors on the lattice. Horizontal bonds contribute with a factor x to the partition function (bond activity), whereas vertical bonds contribute with a factor $xw$, where $w = \exp(-\epsilon/k_B T)$, $T$ being the temperature and $k_B$ the Boltzmann constant. In the limit $w \to 0$ the one dimensional equilibrium polymerization model is recovered[4], since only horizontal bonds are allowed. The solution of this model on the Bethe lattice of coordination number q equal to four leads to a quite surprising result, two different polymerized phases being present in the phase diagram. One of the polymerized

phases corresponds to a saturated phase, since all sites of the lattice are incorporated into the polymer. For q > 4 only one polymerized phase is found in the phase diagram of the Bethe lattice solution.

One may wonder if the result obtained on the Bethe lattice might be due to the type of lattice, or if similar phase diagrams will be obtained on regular lattices. It is therefore of some interest to study the solution of the model in better approximations in order to find out if similar phase diagrams are obtained. So, we solved the model on the Husimi lattice (the core of a Husimi tree)[5], where the results are expected to be closer to the ones on the corresponding regular lattice than the Bethe lattice results.

We consider a model of equilibrium polymerization[2] on a lattice with directional anisotropy. Let us call y the activity of a monomer located at the end of a chain and $x$ the activity of an internal monomer of a chain. Each bond of a chain oriented in a particular direction on the lattice contributes with a factor $w = \exp(-\epsilon/k_B T)$ to the partition function. Thus, the semi-grand partition function may be written

$$Y(x, y, \omega; N) = \sum_{N_p, N_b, N_1, N_\epsilon} (2y)^{N_p} x^{N_b} (1/2)^{N_1} \omega^{N_\epsilon} \Gamma(N_p, N_b, N_1, N_\epsilon; N), \tag{1}$$

where $N_p$ stands for the number of polymers in the configuration, $N_b$ for the number of bonds, $N_1$ for the number of one-site polymers, and $N_\epsilon$ for the number of bonds in the excited direction. The factor $(1/2)^{N_1}$ ensures that one-site polymers are properly counted[6].

For $w = 1$ we expect this model to exhibit a continuou~phase transition between a non-polymerized phase and a polymerized phase in the limit y → 0 for some critical activity $x_c$. In the solution of the model on the Bethe lattice, the critical activity is given by $x_c = 1/(q - 1)$, where q is the coordination number of the lattice[6]. The extension of this solution to $0 \leq w \leq 1$ leads to the existence of an additional polymerized phase in the phase diagram, which is stable for x > 1 and low values of w.

The remainder of this paper is organized as follows: In section II we define the Husimi lattice and indicate how the model may be solved on this lattice in the form of recursion relations whose stable fixed points correspond to stable thermodynamic phases. In section III we obtain the fixed points of the recursion relations and through the study of their stability build the phase diagram of the model. Conclusions and final comments are found in section IV.

## II. Definition of the lattice and determination of the recursion relations

The Husimi tree is a tree built by attaching polygons to each other by their vertices[7]. So, unlike the situation on the Cayley tree, there are closed cycles on the Husimi tree, but they are all of the same size. It should be remarlted that, similarly to what occurs on the Cayley tree, the ratio between the number of surface sites and the total number of sites on the Husimi tree does not vanish in the thermodynamic limit. This anomaly leads us to expect that the thermodynamic behavior of models on this tree should be quite different from the one found on regular lattices, as was verified explicitly for the Ising model on the Cayley tree[8]. Therefore, if we want the solution to be an approximation to the thermodynamic behavior of the model on regular lattices, we should look at the core of the Husimi tree. Following the nomenclature of our earlier work[5], we call this solution the solution of the model on the Husimi lattice.

Since we want our solution to be an approximation to the behavior of the model on the square lattice, we consider a Husimi tree built with squares. In Fig. 1a a Husimi tree with two generations of squares is depicted. In order to obtain recursion relations for the partition function of the model, we define rooted Husimi subtrees, as may be seen in Fig. 1b, so that the whole tree may be built connecting two of those subtrees to a central site. We define the x and y directions as indicated in Fig. 1.
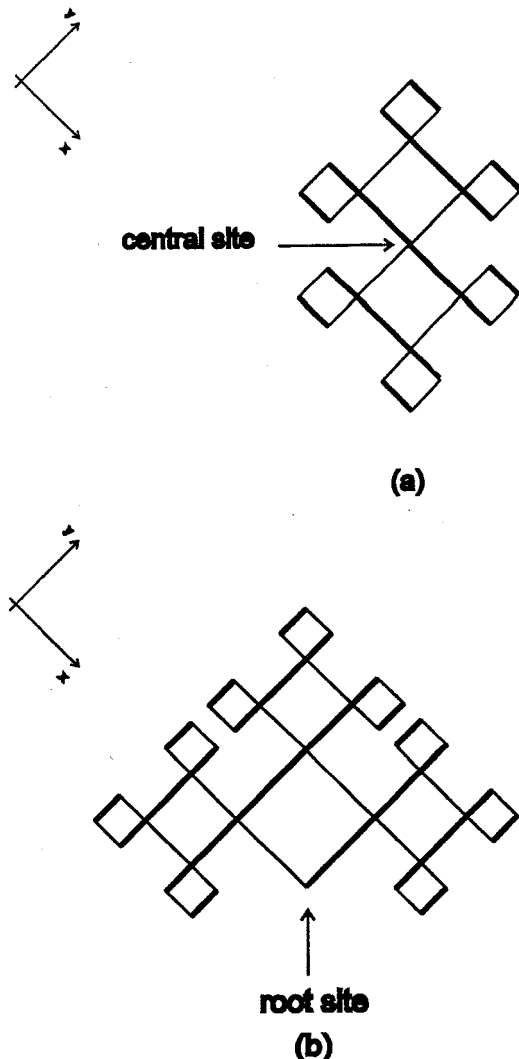


(a)



root site

(b)

Figure 1: (a) Husimi tree with two generations of squares. Bonds with fugacity x are represented by thick lines. (b) Husimi subtree with root site.

We define $g_i(x, w)$ to be the partial partition function of the model on a subtree, where the index i stands for the configuration of the root site of the subtree. There are four possible configurations for this site: 1)

No bond is incident on the root site from above; 2) A bond in the x direction (energy 0) is incident on the root site from above; **3) A** bond in the $y$ direction (energy $\epsilon$) is incident on the root site from above; and 4) Two bonds are incident on the root site from above. These possibilities are drawn in Fig. 2a. Now a sub-

tree with **M + 1** generations may be built attaching three M—generations subtrees to a new root square (see Fig. 2b). It is straightforward to write down recursion relations between the M—generations partial partition functions $g_i$ and the $M+1$-generations partial partition function $g_i'$. The results are

$$g_1' = (g_1 + g_4)^3 + x(g_2 + g_3)^2[(1+\omega)(g_1 + g_4) + \omega x g_1],$$

$$g_2' = x(g_2 + g_3)\{(g_1 + g_4)^2 + x(g_2 + g_3)^2 + \omega x g_1[\omega x g_1 + (g_1 + g_4)]\},$$

$$g_3' = \omega x(g_3 + g_3)\{(g_1 + g_4)^2 + \omega x(g_2 + g_3)^2 + x g_1[\omega x g_1 + (g_1 + g_4)]\},$$

$$g_4' = \omega x^2(g_2 + g_3)^2[(g_1 + g_4) + x(1+\omega)g_1]. \tag{2}$$

Let us define the variables

$$R = \frac{g_2 + g_3}{g_1}, \quad \text{and} \quad S = \frac{g_4}{g_1}; \tag{3}$$

from the recursion relations. As usual in studying mod-

els on treelike lattices[6], it is convenient to introduce ratios between the partial partition functions since they may remain finite in the thermodynamic limit. We obtain the following mapping for R and S

$$R' = xR\{(1+\omega)(1+S)^2 + x(1+\omega^2)R^2 + \omega x[2(1+S) + x(1+\omega)]\}/D,$$

$$S' = \omega x^2 R^2[(1+\omega)(1+S) + \omega x]/D; \tag{4}$$

where the denominator D is given by

$$D = (1+S)^3 + xR^2[(1+\omega)(1+S) + \omega x]. \tag{5}$$

The partition function of the model on the Husimi tree may be obtained considering the operation of attaching two subtrees to the central site. The result is Y = $g_1^2 + 2g_1g_4 + (g_2 + g_3)^2$, which may be rewritten as

$$Y = g_1^2[1 + 2S + R^2]. \tag{6}$$

It should be stressed that the thermodynamic properties of the model which follow from this partition function will be very different from the behavior of the model on regular lattices, since the surface sites dominate the thermodynamic behavior of models defined on the Husimi tree, in a way similar to what happens

on the Cayley tree[9]. Therefore, since we want our solution to be an approximation to the behavior of the model on regular lattices, we concentrate our attention on the densities in the neighborhood of the central site. Let us define two more variables to do this

$$T = \frac{g_2}{g_1}, V = \frac{g_3}{g_1}; \tag{7}$$

so that R = $T + V$, and the following recursion relations may be derived for them

$$T' = xR\{(1+S)^2 + xR^2 + \omega x[(1+S) + x]\}/D,$$

$$V' = \omega x R\{(1+S)^2 + \omega x R^2 + x[(1+S) + \omega x]\}/D. \tag{8}$$
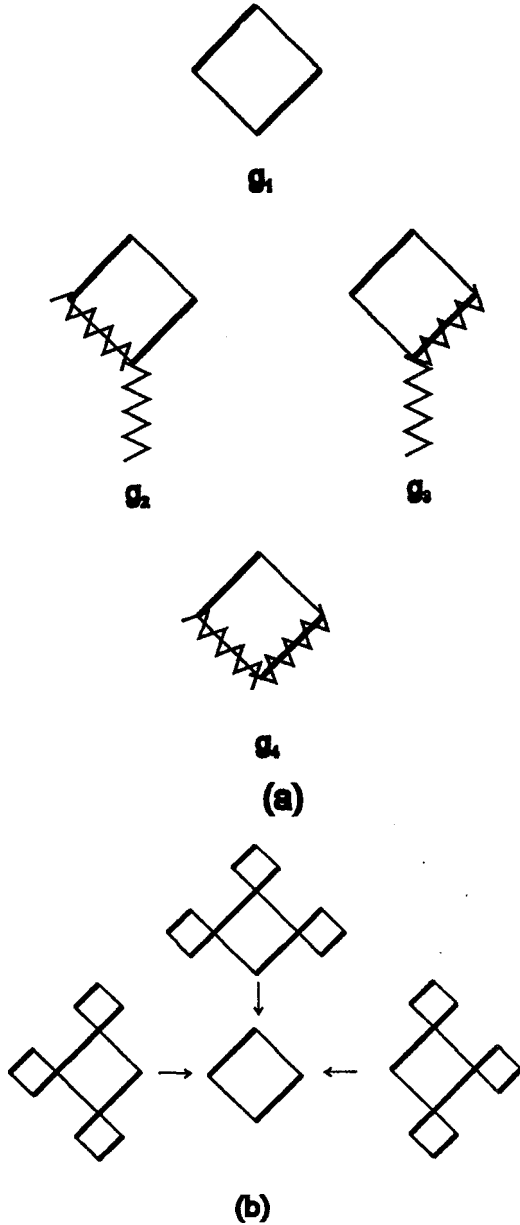
**(a)**



**(b)**

Figure 2: (a) Possible configurations of root site of subtrees and the corresponding partial partition functions. (b) Construction of one subtree with three generations of squares using three two-generations subtrees.

The density of bonds in the non-excited direction $(\rho)$ and the density of bonds in the excited direction $(\rho_\epsilon)$ in the close neighborhood of the central site may then be expressed in terms of the fixed point values of the variables R, S, T, and V, giving

$$\rho = \frac{TR + S}{1 + 2S + R^2},$$

$$\rho_\epsilon = \frac{VR + S}{1 + 2S + R^2}. \qquad (9)$$

Therefore, the thermodynamic properties of the model on the Husimi lattice may be obtained since, for given

values of $x$ and $w$, we may find the stable fixed point values of R, $S$, T, and V, which then allow us to calculate the densities of bonds in the neighborhood of the central site. It is now apparent that any density of physical interest in this neighborhood may be expressed as a function of the ratios S, T, and V. The physical meaning of the ratio variables is apparent from expressions like 9.

### III. Thermodynamic properties of the model

The recursion relations 4 display three fixed points: *1)* A non-polymerized fixed point $R = 0$ and $S = 0$, *2)* A regular polymerized fixed point $R \rightarrow R^*$ and $S \rightarrow S^*$, with $R^*, S^* \neq 0$, and *3)* A Hamilton walk fixed point $R \rightarrow \infty$ and $S \rightarrow S_\infty$. The stability of the first two fixed points may be studied by linearizing the recursion relations in the neighborhood of the fixed points. The same procedure may be used for the third fixed point, after a change of variable $R \rightarrow 1/R$. The results are the following:

*1)* For the non-polymerized fixed point the largest eigenvalue of the *2* x *2* matrix which defines the linearized recursion relations is given by $\lambda_0 = x[(1+w) + \omega x(2 + x + \omega x)]$. This phase is stable in the region of the phase diagram where $\lambda_0 < 1$ and the limit of stability $(\lambda_0 = 1)$ is located at

$$\omega = \frac{\sqrt{(1 + x)^4 + 4x(1 - x)} - (1 + x)^2}{2x^2}. \qquad (10)$$

In this phase, we have $p = \rho_\epsilon = 0$. The stability region of the non-polymerized phase is shown in the phase diagram of the model (Fig. *3*).

*2)* We were not able to solve the fixed point equations of the recursion relations 4 analytically for the regular polymerized fixed point. Thus, we solved them numerically and then found the largest eigenvalue of the matrix. The stability region of this phase is depicted in the phase diagram (Fig. *3*) and to the left the limit of stability of this fixed point is coincident with the limit of stability of the non-polymerized fixed point . Thus, a second order phase transition happens between these two phases.

*3)* When $R$ attains a fixed point at infinity, S tends to the value

$$S_\infty = \frac{\sqrt{(4\omega x^2 + 1)(1+\omega)^2 + 4\omega x(1+\omega)} - (1+\omega)}{2(1+\omega)} \tag{11}$$

The largest eigenvalue of the matrix defining the linearized recursion relations around this fixed point will be given by

$$\lambda_\infty = \frac{2x(1+w^2)}{2\omega x + (1+w) + \sqrt{(1+\omega)^2(4\omega x^2+1) + 4\omega x(1+\omega)}},$$

so that the limit of stability of this phase is located at

$$x = \frac{\omega^3 + \omega^2 + \omega + 1}{\omega^4 - 3\omega^3 + \omega^2 - 3\omega + 1} \tag{12}$$

The densities in this phase are given by

$$\rho = \frac{1}{1+\omega^2}, \quad \text{and} \quad \rho_\epsilon = \frac{w^2}{1+\omega^2} \tag{13}$$

Since $\rho + \rho_\epsilon = 1$ in this phase, all sites of the lattice are incorporated into the polymer, therefore we may call this phase a saturated polymerized phase. Also, we notice that the stability limit of the regular polymerized phase to the right is coincident with the stability limit of the saturated polymerized phase, thus indicating a second order phase transition between those two phases.

All features presented above may be found in the phase diagram depicted in Fig. 3. At $x \to \infty$, the transition between both polymerized phases occurs at $w \simeq 0.3372030$, which should be compared with the corresponding result on the Bethe lattice $w = 0.25$[3]. So, we notice that the region occupied by the saturated polymerized phase in the phase diagram is larger in the Husimi lattice solution than in the Bethe lattice solution, as may also be seen in Fig. 3. Since we expect that the Husimi lattice solution should be a better approximation to the behavior of the model on the square lattice than the Bethe lattice solution, this may be viewed as an indication that the saturated polymerized phase should be present in the phase diagram of the model on the square lattice, being not a result of the approximations we used to study the model.
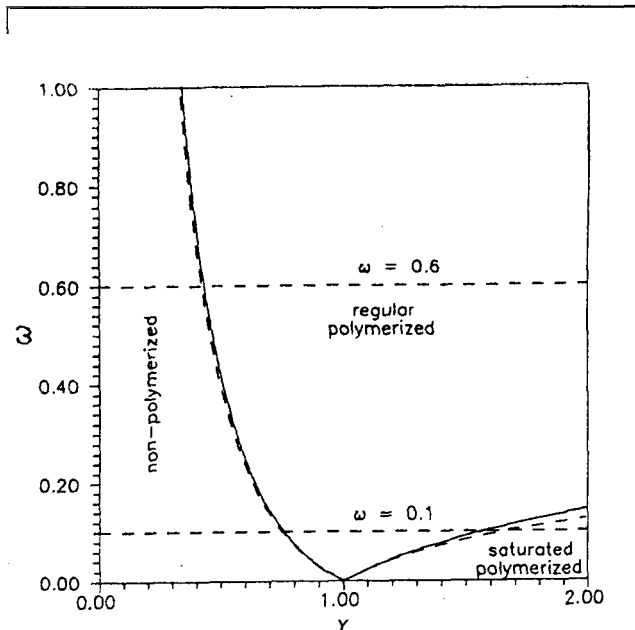


Figure 3: Phase diagram of the model on the Husimi lattice (full lines). The phase boundaries represented by broken lines are Bethe lattice results[3]. The lines $\omega = 0.1$ and $w = 0.6$ are indicated in the diagram, and the densities along these lines are shown in Fig. 4.

In Fig. 4, we show the densities $\rho$ and $\rho_\epsilon$ as functions of the activity x for two values of the variable w. It may be noticed that, for $w \neq 0$, the density $\rho_\epsilon$ does not vanish in the saturated polymerized phase, as happens in the Bethe lattice solution of the model[3].

## IV. Conclusion

In this paper we solve a model for equilibrium polymerization on the Husimi lattice built with squares and whose coordination number is equal to four and with direction-dependent fugacities. The activity of polymer bonds in one direction is equal to x, while
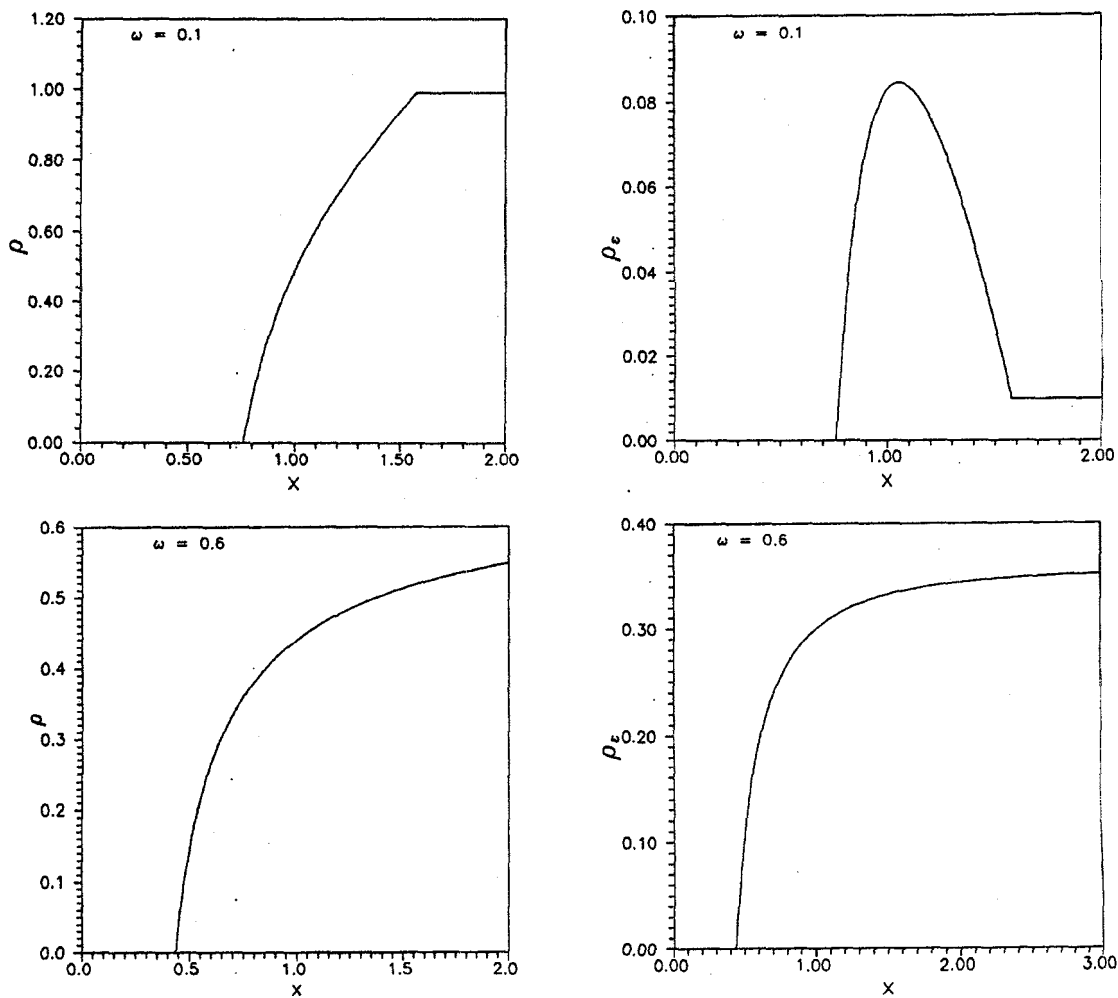
Figure 4: Total density of bonds *(p)* and density of bonds in the excited direction *(p,)* as functions of the fugacity $x$ for fixed values of *w*. For $w = 0.1$ both phase transitions are apparent, whereas for $w = 0.6$ only one transition occurs.

a polymer bond in the other direction of the lattice has an activity equal to $wx$. The problem is reduced to recursion relations whose stable fixed points are associated with thermodynamic phases. Besides a non-polymerized phase, we find two polymerized phases in the phase diagram of the model. One of the polymerized phases has all sites of the lattice visited by the polymer, therefore this phase was called a saturated polymerized phase. In the case where $w = 0$ the model reduces to the one-dimensional equilibrium polymerization model, and our solution is equivalent to the exact solution of this model[4]. The phase transitions between the non-polymerized phase and the regular polymerized phase and between both polymerized phases are of second order, with the exception of the case $w = 0$, where we have a first-order transition between the non-polymerized phase and the saturated polymer-

ized phase. In the saturated polymerized phase, for $w \# 0$, the densities of bonds in both directions are nonvanishing. It should be remarked that the same phase in the Bethe lattice solution of the model has a vanishing density of bonds in the excited direction[3]. The presence of the saturated polymerized phase in the solution of the equilibrium polymerization model on the Bethe an Husimi lattices leads us to the question if a similar phase will occur in the phase diagram of the model on regular lattices, such as the square lattice. This is still an open question. It would be interesting if this matter could be discussed through entropy-energy arguments similar to the Peierls argument[10], but this may not be easy since the equilibrium polymerization model does not exhibit reflection positivity on the square lattice[11]. It may be mentioned that preliminar finite size scaling results for the model on

the anisotropic square lattice indicate the existence of a saturated polymerized phase[12].

## Acknowledgements

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