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Thermodynamic behavior of a polymer with interacting bonds on a square lattice

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Using the transfer matrix technique, finite-size scaling, phenomenological renormalization group, and conformal invariance ideas, the thermodynamic behavior of a polymer with interacting bonds on a square lattice has been studied. In this model, one monomer that belongs to the polymer has an activity $x=e^{\beta\mu}$, while the interactions between bonds of the polymer that are located on opposite edges of elementary squares of the lattice have a statistical weight $y=e^{-\beta\epsilon}$, where ϵ is the interaction energy. Next, the phase diagram of the model in the (x,y) plane was found, which shows three phases, two of them being polymerized. Furthermore, the densities of occupied sites and of bond interactions in each phase were calculated, in order to determine the nature of the transitions between the phases. The results obtained are consistent with a second-order transition line between the nonpolymerized and the regular polymerized phase and a first-order transition between the nonpolymerized and the dense polymerized phase. The boundary between both polymerized phases may be of first or second order, and thus evidence for a tricritical point is found.

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I. INTRODUCTION

Polymers have been extensively studied through models of self-avoiding walks (SAW's) on regular lattices. If we restrict ourselves to two-dimensional lattices, the critical properties of these models have been studied through a variety of techniques, such as series expansions [1], finite-size scaling, and phenomenological renormalization group ideas, in linear noninteracting polymers [2], branched polymers [3], polymers with crossing bonds [4], and interacting polymers [5]. The problem of interacting polymers, in particular, has attracted much attention since the competition between the repulsive excluded volume interactions and the attractive interactions may lead to a collapse of the polymer, usually associated to the θ point. The precise nature of the attractive interactions included in the model may vary. Two possibilities are to associate an interaction energy ϵ to each pair of (i) monomers located on first neighbor sites and not consecutive along the walk and (ii) bonds on opposite edges of elementary squares of the lattice. In general, it is believed that both models should lead to rather similar results, and transfer matrix calculations together with finite-size scaling extrapolations [5] show the collapse transition as a tricritical point, as expected [6]. However, exact Bethe-ansatz calculations for an n-vector model on a chessboard lattice with four-spin interactions among spins located on the edges of colored squares do not fit into this picture. In this particular model, which in the limit $n\rightarrow 0$, is equivalent to SAW's with attractive interactions between bonds on *alternating* squares, the point in the phase diagram that corresponds to the collapse transition is in general not a tricritical point, although its precise nature was not obtained in these calculations [7]. The relation of this model to the one we are considering here will be discussed in more detail in Sec. IV. Some time ago, this contradiction led to an investigation of the solutions of interacting SAW models on Husimi lattices [8], and, while for coordination numbers $q>4$ the usual phase diagram was found as $q=4$, a richer phase diagram is obtained with two distinct polymerized phases. For interacting monomers the collapse transition is a tricritical point in this solution, but for interacting bonds this tricritical point is suppressed and the critical polymerization line ends at a critical endpoint, and, therefore, the phase diagram for this model on the Husimi lattice is consistent with the Bethe-ansatz result for the $n\rightarrow 0$-vector model with four-spin interactions.

In this paper we present an investigation of the phase diagram of SAW's on the square lattice with attractive interactions between bonds, using the transfer matrix method to solve the model exactly on cylinders with different perimeters L and phenomenological renormalization group ideas to extrapolate the results to the two-dimensional limit $L\rightarrow\infty$. Our main purpose is to verify if the qualitative features found in the phase diagram of the model defined on a $q=4$ Husimi lattice are present in the square lattice solution.

Detailing the method we used, we start building a transfer matrix for the model defined on strips of width L and with periodic boundary conditions in the transverse direction, generalizing a method proposed for noninteracting SAW's [2]. The correlation length ξ_L may then be obtained from the eigenvalues of this matrix. This process is repeated for increasing values of L and through an extrapolation process [9], we obtain the phase diagram and critical exponents ν and η for the $L\rightarrow\infty$ case, that is, the square lattice. The basic idea is to use the phenomenological renormalization group (PRG) equation [10],

$$\frac{\xi_L(\alpha)}{L}=\frac{\xi_{L'}(\alpha)}{L'}, \tag{1}$$

and to find the fixed point α^* that solves the equation above,

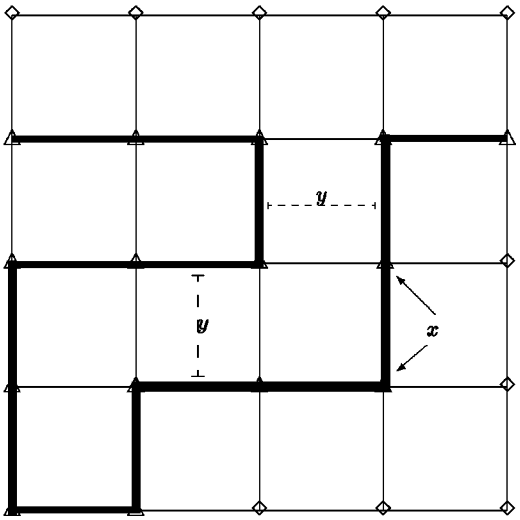

FIG. 1. A possible configuration for a polymer with interacting bonds on the square lattice.

where α is a relevant parameter defined in the model. If we know α^*, the critical exponent ν can be estimated by

$$1+\frac{1}{\nu}=\frac{\ln\left[\frac{d\xi_L(\alpha)}{d\alpha}\Big/\frac{d\xi_{L'}(\alpha)}{d\alpha}\right]\Bigg|_{\alpha^*}}{\ln\left(\frac{L}{L'}\right)}, \tag{2}$$

and the critical exponent η is given by [11,12]

$$\eta\cong\frac{1}{\pi}\frac{L}{\xi_L(\alpha_\infty^*)}, \tag{3}$$

where α_∞^* is the fixed point extrapolated for the square lattice ($L\rightarrow\infty$ limit). The correlation length is obtained from the transfer matrix through [13]

$$\xi^{-1}=\ln\left(\frac{\lambda_1}{\lambda_2}\right), \tag{4}$$

$\lambda_{1,2}$ being the largest and the second largest eigenvalue of the transfer matrix, respectively. We define the model in Sec. II, and Sec. III shows the results and discussions. Conclusions can be found in Sec. IV.

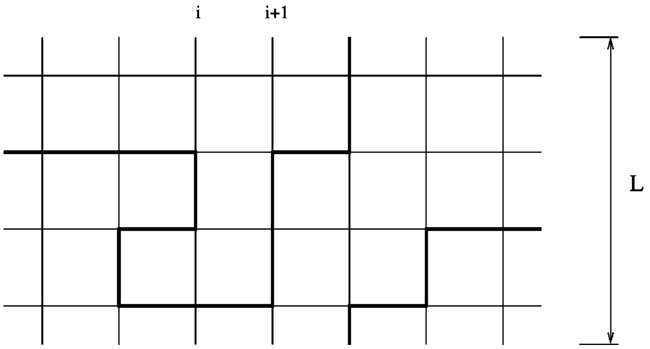

FIG. 2. A strip with $L=4$ with a configuration for a polymer.

II. THE MODEL OF SAW'S WITH INTERACTING BONDS

In order to study the model of a polymer with interacting bonds with periodic boundary conditions on the square lattice (see Fig. 1), we define an activity $x=e^{\beta\mu}$ associated with the monomers that belong to the polymer, and a Boltzmann factor $y=e^{-\beta\epsilon}$ for the interaction between bonds, where ϵ is the interaction energy. Thus, an energy ϵ is associated to each pair of bonds belonging to the polymer that are located on opposite edges of an elementary square (plaquette) of the lattice. If $\epsilon<0$ the interaction is attractive, while for $\epsilon>0$ it is repulsive. When $\epsilon=0$ ($y=1$), we have the noninteracting polymer model, for which there are known results for the critical exponents $\nu=\frac{3}{4}$ and $\eta=\frac{5}{24}$ [14]. We consider strips of width L and infinite length, as shown in Fig. 2, so that a single polymer is supposed to pass through the whole strip. The grand-canonical partition function for the model (the number of monomers incorporated into the polymer fluctuates) [15] is

$$Y=\sum x^{N_x}y^{N_y}, \tag{5}$$

where the sum is over all configurations of the polymer in the strip, N_x is the number of monomers incorporated into the polymer and N_y is the number of opposite pairs of edges in elementary squares that are occupied by bonds of the polymer, so that ϵN_y is the energy associated to the configuration of the polymer.

A transfer matrix may be defined for each width L of the strip and in the thermodynamic limit the adimensional free energy per site will be given by

$$\phi=\lim_{N\rightarrow\infty}\frac{-\ln Y}{N}=-\frac{1}{L}\ln\lambda_1, \tag{6}$$

where λ_1 is the largest eigenvalue of the transfer matrix. The transfer matrix is block diagonal, the first (1×1) block corresponding to the empty lattice, or nonpolymerized phase ($\lambda=1$), and the remaining block for all other configurations. It is this second block of the transfer matrix we consider below. For a pair of widths, L and L', we calculate the correlation length ξ [using Eq. (4)] and then the fixed points x_c of Eq. (1), for a given value of y. Changing y, we can find the whole phase diagram for the pair $L-L'$. We are restricted to $L\leqslant 7$, since the size of the transfer matrix grows very

TABLE I. Number of states N_S of the transfer matrix as a function of L. N_{SBD} is the size of the matrix after a block-diagonalization process.

L	1	2	3	4	5	6	7
N_{SBD}	1	3	9	31	114	442	1777
N_S	1	6	27	124	570	2652	12439

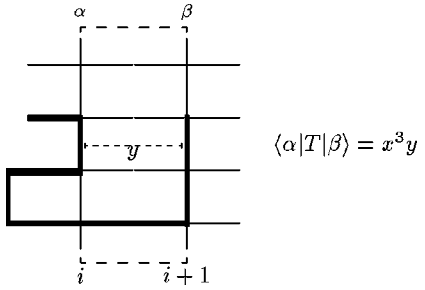

FIG. 3. A possible configuration of the walk between two neighboring sets of horizontal bonds and the corresponding contribution to the transfer matrix.

quickly with L (see Table I), and we have computational limitations. Furthermore, there are parity problems and we are forced to choose $L'=L+2$, so we study the pairs 1–3, 2–4, 3–5, 4–6, and 5–7, obtaining the phase diagrams for each pair of widths. The transfer matrix is built starting from the definition of the connectivity properties of the walk, and this is done according to a prescription introduced by Derrida [2], generalized to take the attractive interactions into account. As an example, we show in Fig. 3 a graphical representation of an element of the transfer matrix. To study the physical properties of the phases in the diagrams, and also the kind of transition between them, we calculate the density of sites (or monomers) incorporated into the polymer (ρ_x) and the density of bond interactions (ρ_y) in the strips. The densities are obtained through

$$\rho_x=\frac{\langle N_x\rangle}{N}=\frac{1}{L}\frac{x}{\lambda_1}\frac{\partial\lambda_1}{\partial x}, \tag{7}$$

and

$$\rho_y=\frac{\langle N_y\rangle}{N}=\frac{1}{L}\frac{y}{\lambda_1}\frac{\partial\lambda_1}{\partial y}. \tag{8}$$

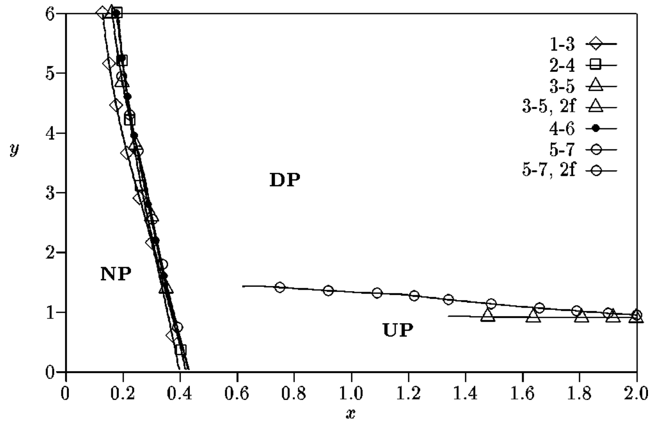

FIG. 4. Phase diagrams obtained for all pair of widths studied. NP is the nonpolymerized phase, UP is the usual polymerized phase and DP is the dense polymerized phase. All are explained in the text.

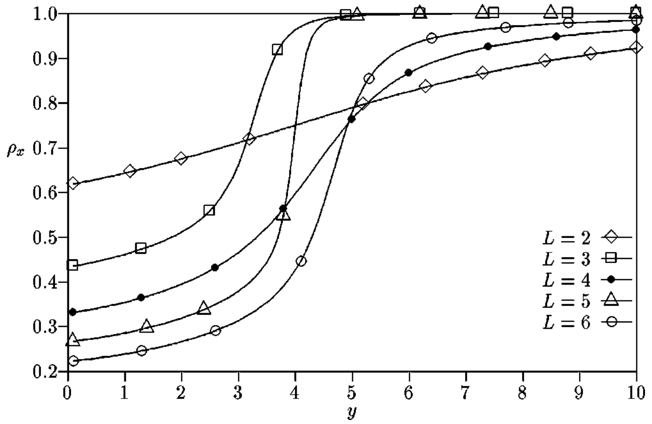

FIG. 5. Density of sites ρ_x for $x=0.2$.

We point out that both densities are normalized, being equal to one for hamiltonian walks, that visit every site of the lattice. Also, the internal energy per site of the model is given by $\epsilon\rho_y$.

III. RESULTS AND DISCUSSIONS

All phase diagrams we obtained are shown in Fig. 4, and there are three phases in the phase diagrams: a nonpolymerized phase (NP), which has $\rho_x(x,y)=0$ and $\rho_y(x,y)=0$ in the whole phase, so there is no polymer on the lattice; a usual polymerized phase (UP), with $0\leqslant\rho_x(x,y)\leqslant1$ and $0\leqslant\rho_y(x,y)\leqslant1$; and a second polymerized phase, in which $\rho_x(x,y)=1$ and $\rho_y(x,y)\approx1$ in the whole phase, so we call this a dense phase (DP). In this phase, all sites of the lattice are visited by the polymer, in a configuration that maximizes the number of the interactions between bonds. The phase diagram of the model of polymers with interacting bonds on the Husimi lattice [8] also shows these three phases.

The transition between the NP phase and the DP phase is of first order, since the values of the densities change from 0 to 1 abruptly. We can see this behavior in Figs. 5 and 6, where we show the densities of monomers and of bond interactions for $x=0.2$ as a function of y. For this value of x, we are in the NP-DP transition region. It should be stressed

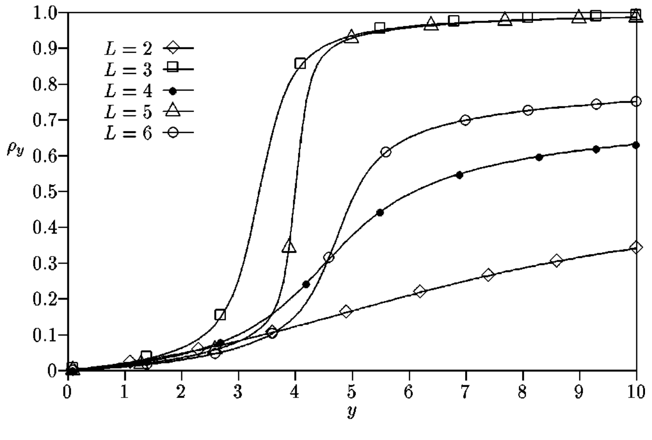

FIG. 6. Density of bond interactions ρ_y for $x=0.2$.

TABLE II. Results obtained for x_c and ν in the NP-UP transition.

L	L'	x_c $(y_c=1)$	ν $(y_c=1)$	x_c $(y_c=1.2)$	ν $(y_c=1.2)$
1	3	0.357100282	0.68778987	0.348073927	0.676736580
2	4	0.369539639	0.73077081	0.358084540	0.711872248
3	5	0.375076826	0.74186350	0.363995791	0.726761201
4	6	0.377291276	0.74621498	0.366642726	0.735815099
5	7	0.378185851	0.74825396	0.367805168	0.741344430
∞[a]		0.37909 ± 0.00004	0.7507 ± 0.0008	0.36919 ± 0.0003	0.7498 ± 0.0004

[a] Results extrapolated for the square lattice.

that in this diagram of a density as a function of a statistical weight and in the ones below, we are considering the block of the transfer matrix that corresponds to one polymer that passes through the whole strip in the longitudinal direction. Thus, the lowest value of ρ_x consistent with the boundary conditions is equal to $1/L$. As expected, the transition is not sharp for finite L, but builds up as the width is increased. If the nonpolymerized block of the transfer matrix is included, the usual NP-UP transition on the strips for $y=1$ is of first order, and the discontinuity in ρ_x at the transition is reduced as L is increased, vanishing in the two-dimensional limit $L\rightarrow\infty$, where the transition turns into a continuous one [16].

The transition NP-UP is of second order, and the point of this frontier that corresponds to noninteracting polymers ($y=1$) was obtained by several techniques [1,2]. One of the best values of this point at the moment is ($x_c=0.379\,052\,27\pm0.000\,000\,12, y=1$) [1]. Our results for this point are shown in Tables II and III, for all pairs $L-L'$, and after extrapolation we found ($x_c=0.379\,09\pm0.000\,04, y=1$). The critical exponents ν and η for this frontier were also calculated. For $y=1$, the values of the exponents should be $\nu=\frac{3}{4}$ and $\eta=\frac{5}{24}=0.208\,333\ldots$ [14], exactly. From universality, we expected that the critical exponents should be the same in all boundary NP-UP. So, we calculate the values of these quantities for $y=1.2$ too, and we obtained $\nu=0.7507\pm0.0008$ and $\eta=0.2082\pm0.0004$, for $y=1$, and $\nu=0.7498\pm0.0004$ and $\eta=0.205\pm0.003$, for $y=1.2$. The exponents remain constant, within the error bars, and, therefore, universality is verified. Tables II and III also show these extrapolated values.

Finally, the transition between the two polymerized phases is more interesting. For large values of x, the transition is of second order, but as x is lowered, there are indications of a discontinuous transition. In the $q=4$ Husimi lattice solution of the model, a tricritical point was found separating these two regimes. Although we tried to locate this point on the boundary between both polymerized phases using methods such as the three widths renormalization [3] [see Eq. (9)], we were not successful. Nevertheless, this does not rule out the possibility of existence of a tricritical point, since we have big limitations in our analysis due to the rather small widths we were able to consider, which are further enhanced by the parity effects present in the problem. The study of the densities of monomers and interactions calculated for strips of increasing width furnishes evidence for the existence of the tricritical point. In order to obtain an estimate of the location of this point we show some plots of these densities. In Figs. 7 and 8 we show the densities for a small value of x ($=0.4$),while in Figs. 9 and 10 the densities for $x=2.4$, a large value, are shown. Both are in the UP-DP transition region. For $x=0.4$ we believe the transition to be of first order, while for $x=2.4$ the transition should be continuous.

We may estimate the location of the tricritical point calculating the functions $\partial\rho_x/\partial y$ and $\partial\rho_y/\partial y$. In the second-order region, these quantities are monotonically decreasing functions of y, while in the first-order region they should diverge in the two-dimensional limit, and thus for finite and sufficiently large L a sharp peak should be found in these quantities. When one behavior changes to another, we have the tricritical point. Our estimate of this point is ($x_{\mathrm{tcp}}=1.5\pm0.1, y_{\mathrm{tcp}}=1.1\pm0.1$). Figures 11 and 12 show these functions for some values of x.

The first-order boundary between the two polymerized phases reaches the frontier between NP and DP phases, which is also of first order. At this point, the critical line between NP-UP phases ends, and thus we have a critical endpoint there. We use the phenomenological renormalization of three widths [3] to estimate the location of this point. This method uses the equation

$$\frac{\xi_L(x^*,y^*)}{L}=\frac{\xi_{L'}(x^*,y^*)}{L'}=\frac{\xi_{L''}(x^*,y^*)}{L''}, \tag{9}$$

TABLE III. Results obtained for exponent η. We used the values of x_c^∞ of Table II in Eq. (3) for each width, and then performed the extrapolation.

L	1	2	3	4	5	6	7	∞[a]
η $(y_c=1)$	0.327775991	0.281475961	0.24990429	0.221282919	0.215882203	0.213115816	0.211526338	0.2082 ± 0.00004
η $(y_c=1.2)$	0.317177926	0.270674229	0.239802629	0.223985085	0.215855055	0.211387646	0.208599364	0.205 ± 0.003

[a] Results extrapolated for the square lattice.

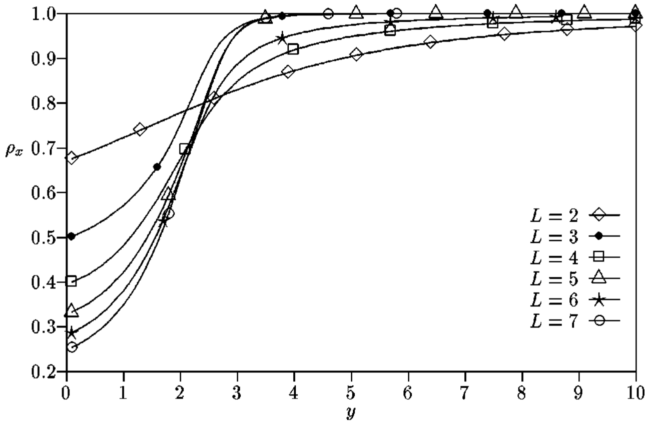

FIG. 7. Density of sites ρ_x for $x=0.4$.

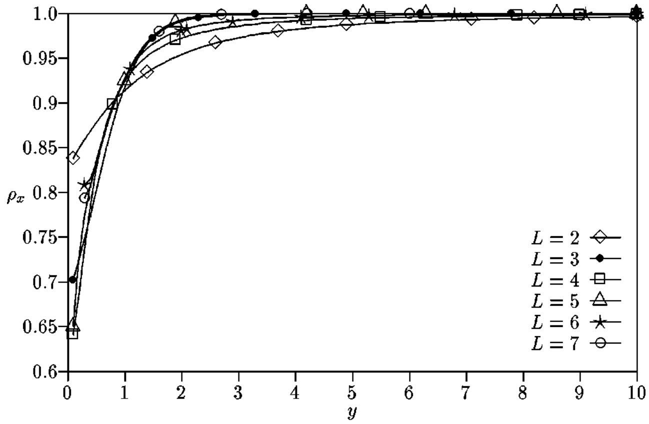

FIG. 9. Density of sites ρ_x for $x=2.4$.

to find higher order critical points (x^*,y^*) (such tricritical or critical endpoints). We found $(x_{\rm cep}=0.244\pm 0.002, y_{\rm cep}=3.86\pm 0.03)$. In Fig. 13 we show a sketch of the phase diagram of the model of interacting bonds on the square lattice.

IV. CONCLUSIONS

Based on the results shown above, we may conclude that the model of interacting bonds on the square lattice has a phase diagram with three phases: a nonpolymerized phase, with $\rho_x=\rho_y=0$; a usual polymerized phase, in which $0\leqslant\rho_x(x,y)\leqslant 1$ and $0\leqslant\rho_y(x,y)\leqslant 1$; and a dense polymerized phase, which has $\rho_x(x,y)=1$ and $\rho_y(x,y)\approx 1$, in the whole phase. The transition is of first order, in the nonpolymerized–dense-polymerized frontier, and, for small x, in the frontier between the two polymerized phases. It is of second order in the nonpolymerized–usual-polymerized frontier, and, for large values of x, in the frontier between the two polymerized phases. Figures 4–12 support these assumptions.

The values of critical exponents on the polymerization line are shown in Tables II and III, and they agree with the expected values, in particular, regarding the universality of the exponents ν and η. It should be mentioned that recently, based on field theoretical arguments, it was speculated that such an universality might break down for the exponent γ, related to the number of SAW configurations, for a model of bond-interacting SAW's where a *direction* is assigned to the SAW and the interaction energy between bonds is chosen to be different for the parallel and antiparallel cases [17]. Although there are conflicting results in the literature concerning evidences for this conjecture [18], it seems now that it actually is not true, as may be concluded through methods similar to the ones we used here [19] and from data furnished through extensive simulations [20]. We found estimates $(x_{\rm tcp}=1.5\pm 0.1, y_{\rm tcp}=1.1\pm 0.1)$ for the tricritical point at the frontier between the two polymerized phases, and $(x_{\rm cep}=0.244\pm 0.002, y_{\rm cep}=3.86\pm 0.03)$ for the critical endpoint, where the critical polymerization line meets the first-order transition line. Figure 13 shows a sketch of the phase diagram for the model defined on the square lattice, and this diagram is qualitatively similar to the one for the same model defined on the Husimi lattice [8]. To our knowledge, the model studied in more detail which is close to the one we are considering here is the n-vector model with four-spin interactions [7], which may be mapped on a model of nonintersecting loops covering the edges of the lattice. In this

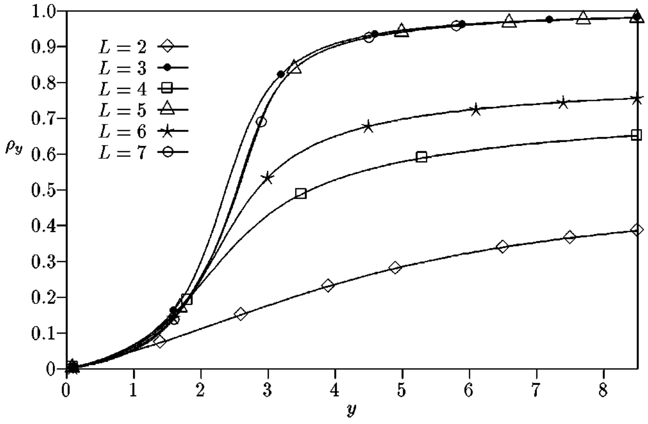

FIG. 8. Density of bond interactions ρ_y for $x=0.4$.

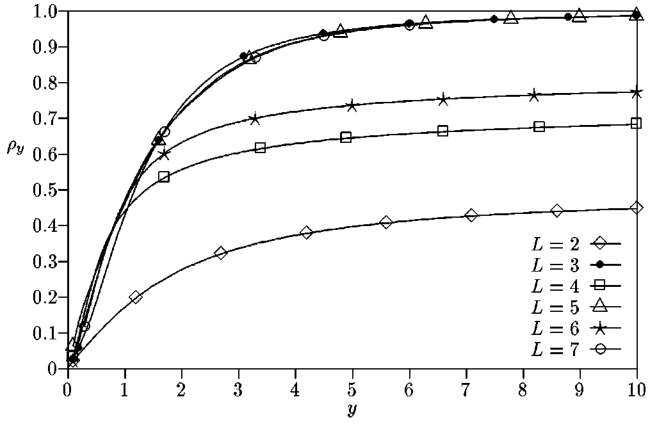

FIG. 10. Density of bond interactions ρ_y for $x=2.4$.

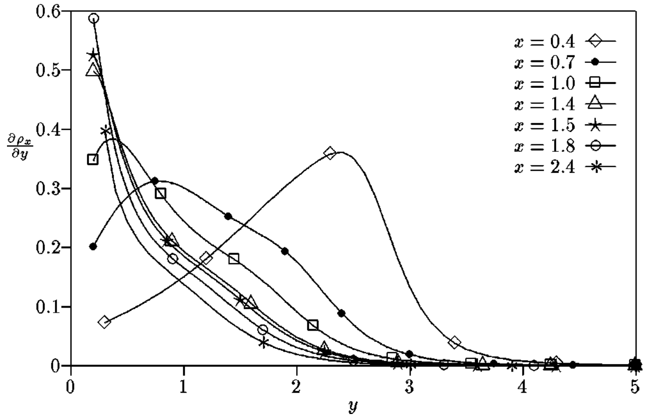

FIG. 11. Function $\partial\rho_x/\partial y$ for some values of x, for $L=5$.

model, the spins are located on the *edges* of the original square lattice. In the limit $n\to 0$, the number of loops vanishes and, therefore, a model for a polymer is recovered. There are two interpretations for the vertex configurations of the model, which are depicted in Figure 14. The first interpretation corresponds to considering the loops drawn on the original lattice. For $w=0$ and $u=v=x$, the model corresponds to the one we considered here when $y=1$, that is, without attractive interactions. The configurations with weight w correspond to the attractive interactions, and they are located *at* a site of the lattice. The four edges incident on these vertices are occupied, and thus in the loop gas model configurations are considered for $w\neq 0$, which are absent in the model we studied here, where four coordinated vertices are not allowed. In the other interpretation of the configurations of the loop gas model the graphs are drawn on the dual square lattice formed by joining the middle points of the edges of the original lattice. In this mapping, four coordinated vertices are absent but for $v\neq 0$ bonds between second neighbors are allowed. Furthermore, on half of the elementary squares (those with a vertex of the original lattice in their centers) only the bond configurations with one (weight u) or two (weight w) bonds are allowed and thus for $v=0$ in this interpretation the loop gas model corresponds to a subset of the configurations allowed in the model we considered. It may be seen in Fig. 14 that the configurations of the polymer in the model we considered may also be specified fixing the bond configurations of each colored elementary square in a chessboard lattice. The loop gas model allows, when $v\neq 0$, for second neighbor bonds in these squares. On the other hand, configurations with two and three occupied edges on colored elementary squares are not allowed in the loop gas model. In conclusion, the model considered here and the loop gas model are not equivalent when attractive interactions are present, although they are physically similar, since in both models the attractive interactions favor more compact configurations.

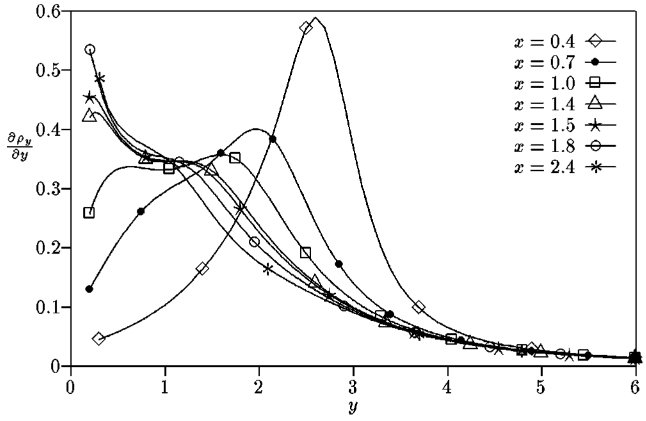

FIG. 12. Function $\partial\rho_y/\partial y$ for some values of x, for $L=5$.

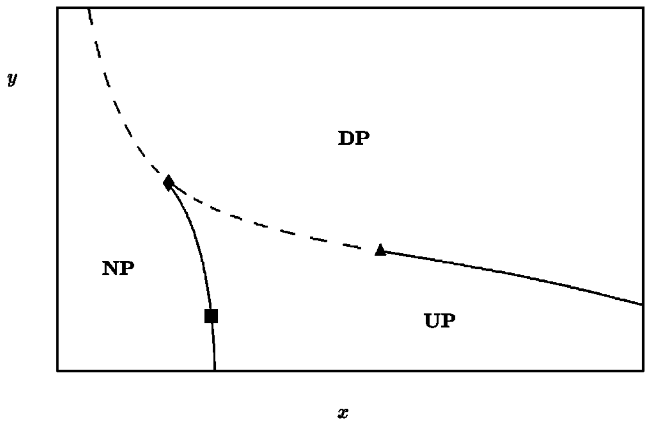

FIG. 13. Sketch of the phase diagram of the model of interacting bonds on the square lattice. Solid lines are second-order transitions, while dashed lines are the first-order ones. ■ is the point $(0.379\,09\pm 0.000\,04,1)$, ♦ represents the critical endpoint $(0.244\pm 0.002,3.86\pm 0.03)$, and ▲ is the tricritical point $(1.5\pm 0.1,1.1\pm 0.1)$.

In general, the phase diagram of the $n\to 0$ loop gas model

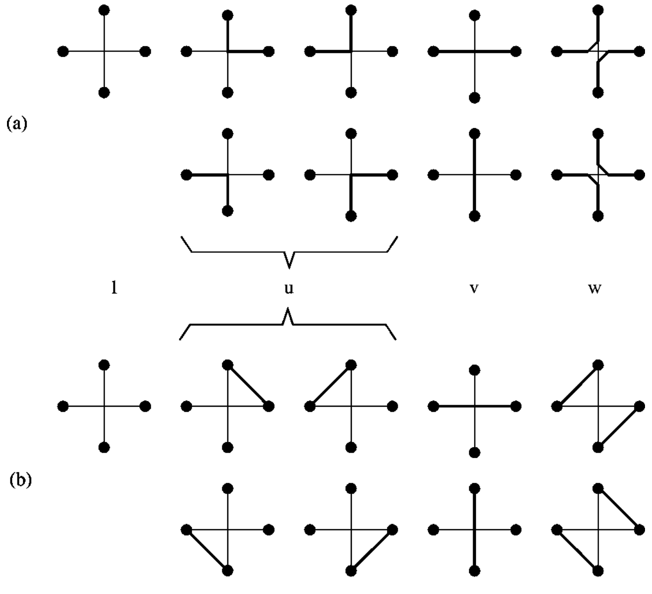

FIG. 14. Vertex configurations of the interacting loop gas model on (a) the original square lattice and (b) the dual square lattice built by joining the middle points of the edges of the original lattice. The Boltzmann weights of the configurations are indicated.

in the $(u=v,w)$ plane is quite similar to the one found here in the (x,y) plane (Fig. 13). As pointed above, the models are not equivalent and thus a quantitative comparison of the phase diagrams is not possible. In the loop gas model, the phase we call dense polymerized here is absent for $v=0$, and in this case the critical polymerization line ends at a tricritical point [21], which may be identified with the θ point.

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