Nature of the Collapse Transition for Polymers

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We solve models for self-avoiding walks on Husimi lattices of coordination number $q = 2(\sigma + 1)$, $\sigma = 1, 2, \ldots$ made up of squares. An attractive interaction is introduced between first-neighbor sites incorporated into the walk or between bonds on opposite edges of elementary squares. For $\sigma > 1$ one polymerized phase is present in the phase diagram and the Θ point is a tricritical point. For $\sigma = 1$, however, two distinct polymerized phases appear, and the Θ point is a tricritical point (attractive sites) or a critical end point (attractive bonds).

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Self-avoiding walks on lattices have been used as models for polymers for quite a long time [1]. In the case of polymers diluted in poor solvents, the effect of the solvent-monomer interactions may be included in such models through the addition of an attractive interaction between monomers on first-neighbor sites incorporated into the polymer which are not consecutive monomers along the chain [2]. In this model, there is a competition between the repulsive excluded volume interactions and the attractive interactions, so that for sufficiently large attractive interactions the second order polymerization transition turns into first order. On the first order line the nonpolymerized phase coexists with a collapsed polymerized phase. The tricritical point of the phase diagram where the order of the transition changes is called the collapse transition and may be associated with the Θ point [2]. On two-dimensional lattices, however, there are indications that the phase diagram of this model has different features. Numerical transfer-matrix calculations [3] and exact Bethe-ansatz results [4,5] for an $O(n)$ model on the square lattice with four-spin interactions lead to a phase diagram where the point which corresponds to the Θ point is a multicritical point, whose precise nature is not clear from these calculations. In the limit $n \to 0$ this model corresponds to self-avoiding walks with attractive interactions between bonds of the walk located at opposite edges of elementary squares of the lattice. On the other hand, transfer matrix calculations for self-avoiding walks on the square lattice with attractive interactions between monomers seem to be consistent with a tricritical Θ point [6]. The exact values for the tricritical exponents on two-dimensional lattices were proposed from the study of self-avoiding walks on a dilute honeycomb lattice [7] and the conformal invariance properties of the tricritical $n \to 0$ model were also studied [8].

Here we solve two models of interacting self-avoiding walks, with attractive interactions between monomers and bonds, respectively, on Husimi lattices [9,10], built with squares and of arbitrary ramification of squares σ, so that the coordination number is equal to $q = 2(\sigma + 1)$. We find the properties of the models in the core of the Husimi tree (Husimi lattice), rather than solving the models on the tree itself. It is known that, due to the fact that the number of surface sites is of the same order as the total number of sites in the Husimi tree, thermodynamic properties of models solved on this tree may show features which are quite different from the ones found in solutions on regular lattices [10]. On the other hand, solutions on the Husimi lattice may be good approximations to the thermodynamic properties on real lattices. Although the solution of a model on the Husimi lattice displays classical exponents, it may show features of the phase diagram which are not present in usual mean-field calculations [11]. The phase diagrams we obtain are qualitatively different for $\sigma = 1$ ($q = 4$) and for $\sigma > 1$ ($q > 4$). In the former case, two distinct polymerized phases are present and in the latter case we find just one polymerized phase. For $\sigma = 1$ there are differences in the phase diagrams of the models with attractive monomers and with attractive bonds; in the first case the critical polymerization line ends at a tricritical point, whereas in the second case it finishes at a critical end point. If we admit that these features occur for the solution of the model on the square lattice, the apparent contradiction regarding the nature of the Θ point between the Bethe-ansatz results for the $O(n)$ model and the transfer matrix results for the model of self-avoiding walks with attractive monomer-monomer interactions is solved.

We consider self-avoiding walks on a hypercubic lattice, whose end points are on the boundary of the lattice, associating an activity x to each bond of the walk. For the model with attracting monomers, a Boltzmann factor $\omega = \exp(-\epsilon/k_B T)$ corresponds to each pair of sites of the walk which are located on first-neighbor sites of the lattice but are not consecutive along the walk. For the model with attracting bonds, the weight ω is associated with each pair of bonds of the walk which are located on opposite edges of an elementary square of the lattice. So the grand partition function of the model on a lattice of N sites may be written

$$Y(x,\omega;N) = \sum x^{N_b}\omega^{N_i}, \tag{1}$$

where N_b is the number of bonds of the configuration, N_i is the number of interacting pairs of sites or bonds of the walk, and the sum is over all configurations with self-avoiding walks on the N-site lattice whose end points are located on the boundary of the lattice. On the square lattice, the model with bond interactions only in alternating squares is equivalent to the $n \to 0$ limit of the n-vector model considered in Refs. [3–5], with the Hamiltonian

$$\frac{-\mathcal{H}}{k_B T} = K_2 \sum_{\langle i,j\rangle} \vec{S}_i \cdot \vec{S}_j + K_4 \sum_{sq} [(\vec{S}_1 \cdot \vec{S}_2)(\vec{S}_3 \cdot \vec{S}_4) + (\vec{S}_1 \cdot \vec{S}_4)(\vec{S}_2 \cdot \vec{S}_3)], \tag{2}$$

where the n-component vectors $\vec{S}$ are located on the sites of a square lattice, the first sum is over all first-neighbor pairs of vectors and the second sum is over groups of four vectors on vertices of colored squares, if we imagine the square lattice as a checkerboard. Both models are equivalent if

$$\begin{aligned} x &= K_2, \\ (\omega - 1)x^2 &= K_4. \end{aligned} \tag{3}$$

The model with attractive monomers is not equivalent to such a simple n-vector model in the limit $n \to 0$.

To solve the models defined above on the Husimi lattice [10], we consider subtrees with a ramification of squares equal to σ and perform the operation of building a subtree with $M + 1$ generations by connecting three sets of σ M-generation subtrees to the vertices of a new root square (see Fig. 1). Let us denote as g_i, $i = 0,1,2$, the partial partition functions of a subtree with i bonds of the walk incident upon the root site. Defining $a \equiv g_1/g_0$ and $b \equiv g_2/g_0$, we get the following relations for a' and b' of an $(M + 1)$-generation subtree, as functions of a and b of an M-generation tree, for the model with attractive monomers:

$$\begin{aligned} a' &= \frac{2xf(1 + 2\omega h + \omega^3 h^2 + x + x\omega^2 h + x^2\omega + x\omega^2 f^2)}{1 + 3h + (1 + 2\omega)h^2 + \omega^2 h^3 + 2xf^2(1 + \omega h) + x^2 f^2}, \\ b' &= \frac{x^2 f^2(1 + 2x\omega + \omega^2 h)}{1 + 3h + (1 + 2\omega)h^2 + \omega^2 h^3 + 2xf^2(1 + \omega h) + x^2 f^2}, \end{aligned} \tag{4}$$

where $f = \sigma a$ and $h = \sigma b + \frac{\sigma(\sigma-1)}{2}a^2$. For attractive bonds the result is

$$\begin{aligned} a' &= \frac{2xf[(1 + h)^2 + x(1 + h) + x^2\omega + x\omega f^2]}{(1 + h)^3 + 2xf^2(1 + h) + x^2 f^2}, \\ b' &= \frac{x^2 f^2(1 + 2x\omega + h)}{(1 + h)^3 + 2xf^2(1 + h) + x^2 f^2}. \end{aligned} \tag{5}$$

In the thermodynamic limit $M \to \infty$, the variables a and b approach stable fixed point values which correspond to stable thermodynamic phases.

In order to calculate the densities of bonds ρ_b and the density of monomer-monomer or bond-bond interactions ρ_i in the central square of the tree (see Fig. 1), we consider the operation of connecting four sets of σ

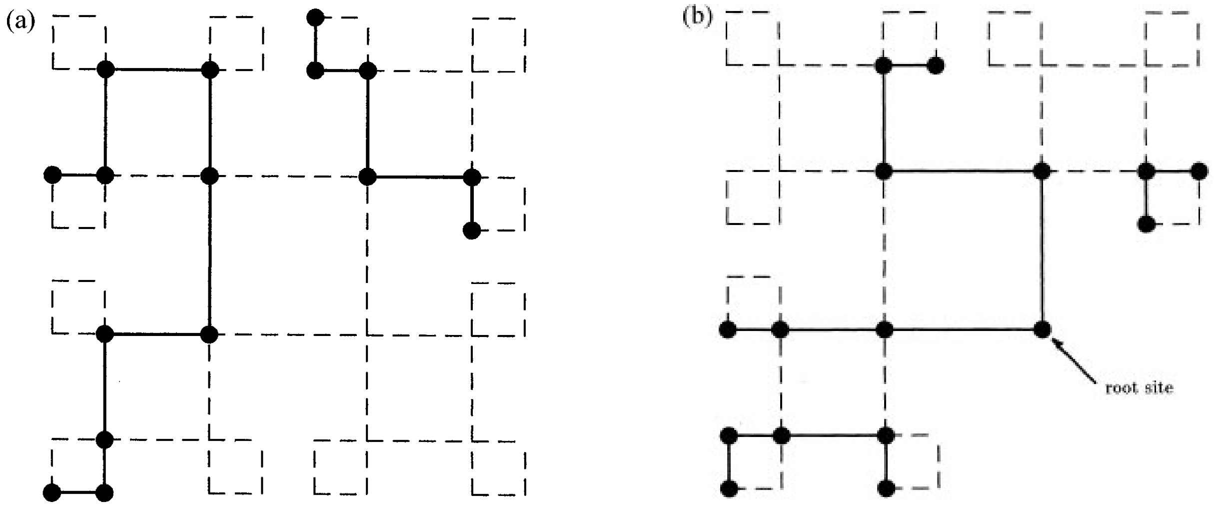

FIG. 1. (a) A Husimi tree with $\sigma = 1$ and three generations with two polymers on it. (b) A subtree with $\sigma = 1$. The configuration shown contributes to the partial partition function g_1 with a term $x^{13}\omega^4$ for the interacting monomer model and $x^{13}\omega^2$ for the interacting bond model.

subtrees to the vertices of this square. The result for attractive monomers is

$$\begin{aligned}\rho_b &= \frac{4xf^2(1 + 2\omega h + \omega^3h^2 + x\omega^2f^2 + 3x^2\omega)}{d}\,,\\ \rho_i &= \frac{4\omega(h^2 + 2xhf^2 + x^3f^2 + 2\omega h^3 + x^2f^4\omega + 3x\omega^2f^2h^2 + \omega^3h^4)}{d}\,,\end{aligned} \tag{6}$$

where

$$\begin{aligned}d = 1 &+ 4h + 2h^2 + 4\omega h^2 + 4\omega^2h^3 + w^4h^4 + 4xf^2\\ &+ 8x\omega f^2h + 4x\omega^3f^2h^2 + 2x^2f^4\omega^2 + 4x^3\omega f^2.\end{aligned}$$

For attractive bonds, we get

$$\begin{aligned}\rho_b &= \frac{4xf^2[(1 + h)^2 + x\omega f^2 + 3x^2\omega]}{(1 + h)^4 + 4xf^2(1 + h)^2 + 2x^2\omega f^4 + 4x^3\omega f^2}\,,\\ \rho_i &= \frac{2x^2f^2(\omega f^2 + 2x\omega)}{(1 + h)^4 + 4xf^2(1 + h)^2 + 2x^2\omega f^4 + 4x^3\omega f^2}\,.\end{aligned} \tag{7}$$

It should be mentioned that these densities are not normalized. Thus, the maximum number of bonds in the central square is equal to 3, so this is the upper limit of ρ_b. Also, the number of interactions in the central square is limited to 4 for attractive monomers and to 1 for attractive bonds, so these are upper limits for ρ_i in both cases.

The phase diagrams are obtained finding the stable fixed points of the recursion relations (4) and (5). For $\sigma > 1$ we find two fixed points: (i) unpolymerized ($a = 0$, $b = 0$) and (ii) regular polymerized ($a, b \neq 0$ and finite). For $\sigma = 1$, however, a saturated polymerized fixed point ($a \to \infty$, $b \neq 0$) is stable in certain regions of the phase diagram. In this phase $\rho_b = \rho_i = 2$ for attractive monomers and $\rho_b = 2$, $\rho_i = 1$ for attractive bonds, and the central square of the tree is found in a configuration with two bonds on opposite edges. We found the stability limits of each fixed point in the x-ω plane. Coincident stability limits of two phases indicate second order transitions and regions where two phases are stable signal a first order transition, whose location may be found through a Maxwell construction [12]. The phase diagrams are shown in Fig. 2 for $\sigma = 1$, which corresponds to a four coordinated Husimi tree. For the model with attracting sites, the polymerization transition is of second order at $\omega = 1$ and turns into a first order transition at the tricritical point located at $x \simeq 0.32774$, $\omega \simeq 1.84193$. The boundary between both polymerized phases is of second order, and ends at a critical end point at $x \simeq 0.24987$, $\omega \simeq 2.82996$. When the attractive interaction is between bonds, the phase diagram changes qualitatively. The second order polymerization transition ends at a critical end point, located at $x \simeq 0.28053$, $\omega \simeq 6.35335$. The transition between both polymerized phases is of second order for large values of x, and changes to first order at a tricritical point located at $x \simeq 0.37628$, $\omega \simeq 4.60326$. When $\sigma = 2$, both models show just one stable polymerized phase, separated from the nonpolymerized phase by a boundary which starts as a second order line for low values of ω and turns into a first order line at a tricritical point.

In conclusion, we obtained the solution of self-avoiding walks with interactions between monomers or bonds on Husimi lattices built with squares. In the case of the four coordinated lattice, we found an additional saturated

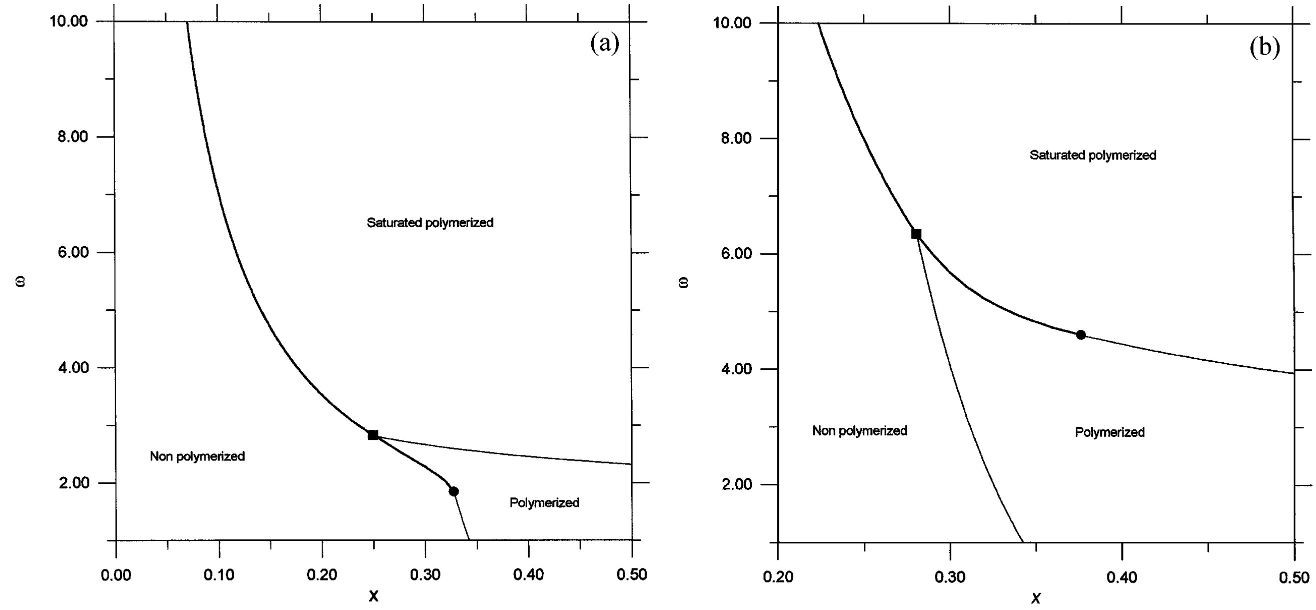

FIG. 2. Phase diagrams for the models with (a) interacting monomers and (b) interacting bonds. The thin lines are second order transitions and the thick lines are coexistence lines. Tricritical points are indicated by circles and critical end points by squares.

polymerized phase in which every site of the lattice is incorporated into the polymer, thus being given by an interacting Hamiltonian walk. Semiflexible Hamiltonian walks have been used to describe polymer melting [13]. The polymerization line ends at a tricritical point for the interacting monomer model and at a critical end point for the interacting bond model. This picture is consistent with both finite size scaling results for the interacting monomer model on the square lattice [6] and exact results for the interacting bond model on the square lattice [5]. One physical argument to understand the situation is that the attractive interaction between monomers is more effective than the one between bonds in promoting the collapse of the polymers, since in the latter case it is necessary, for the interaction to exist, that two bonds of the polymer(s) be located on opposite edges of the same elementary square, whereas in the former case it is sufficient to have two monomers on first-neighbor sites. This may be seen in the configuration shown on the subtree in Fig. 1. Thus, for any value of σ the tricritical Θ point is located at lower values of ω for the interacting monomer model than for the interacting bond model. For $\sigma = 1$ and interacting bonds, the tricritical point is inhibited due to the presence of the saturated polymerized phase. The appearance of additional polymerized phases in the Husimi lattice solution of polymer models was found also for cross-linked polymers [14], branched polymers [15], and polymers on anisotropic lattices [16]. The results presented here open the possibility that the nature of the collapse transition for two-dimensional lattices may depend on the details of the model. Although the scaling properties of polymer chains close to the Θ point were investigated experimentally both in three [17] and in two dimensions [18], these studies were performed with chains of fixed length, and the comparison with the results presented here is not straightforward. One possible experimental situation which could be described by models related to the one considered here would be equilibrium polymerization in a solution [19], which describes experimental results of polymerization of sulfur in organic solvents [20]. As a final remark, we mention that the problem of *directed* polymers with interacting bonds was studied on the square lattice and many features of the phase diagram were found exactly [21]. The Θ point in this diagram is a multicritical point, but the details are quite different from the one presented here. For this model, a polymerized phase of zero density of monomers occupies a finite region of the diagram, even for $\omega = 1$. This seems quite unlikely to happen for regular polymers.

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