

## Exact Results for the Adsorption of a Flexible Self-Avoiding Polymer Chain in Two Dimensions

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We derive the exact critical couplings  $(x^*, y_a^*)$ , where  $y_a^*/x^* = \sqrt{1 + \sqrt{2}} = 1.533\dots$ , for the polymer adsorption transition on the honeycomb lattice, along with the universal critical exponents, from the Bethe ansatz solution of the  $O(n)$  loop model at the special transition. Our result for the thermal scaling dimension, and thus the crossover exponent  $\phi = \frac{1}{2}$ , is in agreement with an earlier result based on conformal invariance arguments. Our result for the geometric scaling dimensions confirms recent conjectures that they are given by  $h_{\ell+1,3}$  in the Kac formula.

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A long flexible polymer in a good solvent with an attractive short-range force between the polymer and the container wall is known to undergo an adsorption transition [1–4]. A standard model for this phenomenon is a self-avoiding walk (SAW) on a  $d$ -dimensional lattice interacting with a  $(d - 1)$ -dimensional substrate. In the lattice model, the SAW has a Boltzmann weight  $x$  per monomer (in the bulk), with weight  $y$  per adsorbed monomer (on the substrate). At the adsorption transition  $y_a^*$  the number of adsorbed monomers scales with the total length  $L$  as  $L_a \sim L^\phi$ , where  $\phi$  is a crossover exponent. The polymer is in the adsorbed phase for  $y > y_a^*$  and the desorbed phase for  $y < y_a^*$ , where the surface attractions are not effective. In the language of surface critical phenomena, the adsorption transition is a *special* transition [5].

Two-dimensional polymers are not without experimental interest [6] and the above model has been widely studied via a number of techniques (see, e.g., [4], and references therein). These include transfer matrix calculations [7], series expansions [8], and a scanning Monte Carlo method [9]. In two dimensions there is a wealth of exact results for the *ordinary* surface transition ( $y < y_a^*$ ) from conformal invariance arguments [4,10–12] and more recently from exact Bethe ansatz calculations [13]. More generally, these results have been obtained for the  $O(n)$  model, from which the configurational properties of SAWs follow in the  $n \rightarrow 0$  limit [1].

The situation is not so clear for the special transition. There is a conformal invariance result for the thermal scaling dimension  $X_\epsilon$ , which leads to the crossover exponent  $\phi = \frac{1}{2}$  [14]. However, the two-variable nature of the special transition poses problems for numerical studies, as errors in the estimates of the critical exponents are compounded by errors in the location of the critical point  $(x^*, y_a^*)$ . Recent simulations on the square lattice have indicated a result significantly larger than the conjectured  $\phi$  value [9].

Here we derive the exact critical couplings  $(x^*, y_a^*)$  for the polymer adsorption transition on the honeycomb lattice, along with the universal critical exponents, from

the Bethe ansatz solution of the  $O(n)$  loop model at the special transition.

Our starting point is the partition function of an  $O(n)$  loop model [15] defined on the honeycomb lattice depicted in Fig. 1,

$$Z_{\text{loop}} = \sum x^L y^{L_s} n^P, \quad (1)$$

where the sum is over all configurations of closed and nonintersecting loops. Here  $P$  is the total number of closed loops of fugacity  $n$  in a given configuration. In the limit  $n \rightarrow 0$  this reduces to the required SAW generating function, with  $x$  the fugacity of a step in the bulk and  $y$  the fugacity of a step along the surface. Here  $L$  is the length of a walk in the bulk and  $L_s$  is the length of a walk along the surface of the strip.

The partition function can be conveniently rewritten in terms of the Boltzmann weights of the empty vertices. To do this we need to distinguish between three classes of vertices:  $\succ$  and  $\prec$  which appear (i) in the bulk and (ii) on the surface, and (iii)  $\rangle$  and  $\langle$  on the surface. For each class we define the weights  $t_b$ ,  $t_{\bar{b}}$ , and  $t_s$ , respectively. We then consider

$$Z_{\text{loop}} = \sum t_b^{\mathcal{N}_b - L_b} t_{\bar{b}}^{\mathcal{N}_{\bar{b}} - L_b - L_s/2} t_s^{\mathcal{N}_s - L_s/2} n^P, \quad (2)$$

where  $\mathcal{N}_b$ ,  $\mathcal{N}_{\bar{b}}$ , and  $\mathcal{N}_s$  are the total numbers of vertices (either full or empty) of class (i), (ii), and (iii). Apart from

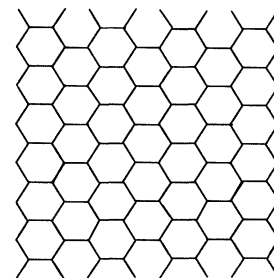


FIG. 1. The open honeycomb lattice.

harmless normalization factors, the two partition functions are equivalent if  $t_b = t_{\bar{b}}$ , along with the identification

$$x = 1/t_b, \quad y = 1/\sqrt{t_{\bar{b}}t_s}, \quad (3)$$

where  $L = L_b + L_{\bar{b}}$ .

The configurations of the loop model can be mapped to those of a three-state vertex model in the standard way [16–18]. The allowed arrow configurations and their corresponding Boltzmann weights are shown in Fig. 2. Here the phase factors are such that  $n = s + s^{-1} = -2 \cos 4\lambda$ . The integrable bulk weights of this honeycomb lattice model are known to follow in a particular limit of the Izergin-Korepin model—a more general three-state model defined on the square lattice [18,19].

For the open boundary conditions of interest here, the integrability of the vertex model can be examined in a systematic way by making use of reflection or  $K$  matrices which satisfy the boundary version of the Yang-Baxter equation. In order to do this, we adapted the Sklyanin construction of commuting transfer matrices [20] to the present geometry [21–23]. In particular, we found that the known diagonal reflection matrices for the Izergin-Korepin model [24] lead to two integrable sets of boundary weights which preserve the  $O(n)$  symmetry [22,25]. For each case  $t_b = t_{\bar{b}} = 2 \cos \lambda$ . Thus from (3) the critical bulk fugacity is

$$1/x^* = \sqrt{2 \pm \sqrt{2 - n}}, \quad (4)$$

which is the well-known bulk critical value [16]. The SAW point occurs at  $\lambda = \pi/8$ , where  $x^* = 1/\sqrt{2 + \sqrt{2}} = 0.541196\dots$

The two integrable sets of boundary weights are [22]

$$t_s = \frac{\sin 2\lambda}{\sin \lambda}, \quad (5a)$$

$$t_s = \frac{\cos 2\lambda}{\cos \lambda}. \quad (5b)$$

Thus from (3) case (5a) gives the critical surface fugacity  $y_0^* = x^*$  and corresponds to an integrable point on the ordinary transition line. However case (5b) is new, and corresponds to the special transition, with

$$y_a^* = (2 - n)^{-1/4}, \quad (6)$$

in the so-called dilute phase  $0 \leq \lambda \leq \pi/4$  ( $-2 \leq n \leq 2$ ). In contrast the surface coupling is complex valued in the dense phase ( $\pi/4 < \lambda \leq \pi/2$ ). We thus confine

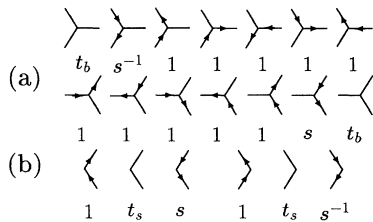


FIG. 2. The allowed arrow configurations and corresponding Boltzmann weights for (a) bulk and (b) surface vertices.

our attention here to the dilute region applicable to the adsorption transition. At  $n = 0$  we have  $y_a^* = 2^{-1/4} = 0.840896\dots$ . This exact result should prove to be a valuable benchmark for future numerical studies of the adsorption transition. For  $n = 1$  the special transition is located at  $y_a^* = 1$  which corresponds to infinitely strong surface couplings, as expected. Our result is also consistent with a recent argument that although there is no special transition for the Ising model, there is a special transition in the geometrical  $O(n)$  model for  $n \geq 1$  [26]. We see from (6) that the critical coupling diverges at  $n = 2$ , and becomes complex for  $n > 2$ .

The central charge  $c$  and scaling dimensions  $X_i$  defining the critical behavior of the model follow from the dominant finite-size corrections to the transfer matrix eigenvalues [27–29]. The central charge follows from the free energy per site,  $f_N = N^{-1} \ln \Lambda_0$ , via

$$f_N \simeq f_\infty + \frac{f_s}{N} + \frac{\pi \zeta c}{6N^2}. \quad (7)$$

Here  $f_s$  is the surface free energy and  $\zeta = \sqrt{3}/2$  is a lattice-dependent scale factor. The scaling dimensions are related to the inverse correlation lengths via

$$\xi_i^{-1} = \ln(\Lambda_0/\Lambda_i) \simeq 2\pi \zeta X_i/N. \quad (8)$$

A set of scaling dimensions of interest appear in the so-called watermelon correlator, which measures the geometric correlation between  $\ell$  noninteracting SAWs tied together at their extremities  $x$  and  $y$ , which for surface critical phenomena are near the boundary of the half-plane [12]. It has a critical algebraic decay,

$$G_\ell(x - y) \sim |x - y|^{-2X_\ell}. \quad (9)$$

These scaling dimensions are associated with the largest eigenvalue in each sector of the transfer matrix. In particular, the spin-spin correlation is related to  $X_1$ . On the other hand, the thermal scaling dimension  $X_\epsilon$ , corresponding to the energy-energy correlation, is related to an excitation in the largest sector of the transfer matrix. Given  $X_1$  and  $X_\epsilon$ , the surface critical exponents follow from [4,5]

$$X_1 = \eta_{||}/2 = \beta_1/\nu = [2 + (\gamma - 2\gamma_1)/\nu]/2, \quad (10)$$

$$X_\epsilon = 1 - \phi/\nu. \quad (11)$$

In terms of the more standard parameter  $g$ , where  $4\lambda + \pi g = 2\pi$ , the bulk exponents  $\gamma$  and  $\nu$  are given by [16]

$$\nu = \frac{g}{4(g-1)}, \quad \gamma = (\frac{3}{4}g + 1/g)\nu. \quad (12)$$

For case (5b), at the special transition ( $x^*, y_a^*$ ) we have obtained the Bethe ansatz solution for the eigenvalues of the transfer matrix [22],

$$\Lambda = \prod_{j=1}^m \frac{\sinh(u_j + i3\lambda/2) \sinh(u_j - i3\lambda/2)}{\sinh(u_j + i\lambda/2) \sinh(u_j - i\lambda/2)}, \quad (13)$$

where the  $u_j$  follow as roots of the Bethe ansatz equations

$$\left[ \frac{\cosh(u_j - i\lambda/2)}{\cosh(u_j + i\lambda/2)} \right]^2 \left[ \frac{\sinh(u_j - i\lambda/2) \sinh(u_j - i3\lambda/2)}{\sinh(u_j + i\lambda/2) \sinh(u_j + i3\lambda/2)} \right]^N = \prod_{\substack{k=1 \\ \neq j}}^m \frac{\sinh(u_j - u_k + i\lambda) \sinh(u_j + u_k + i\lambda) \sinh(u_j - u_k - i2\lambda) \sinh(u_j + u_k - i2\lambda)}{\sinh(u_j - u_k - i\lambda) \sinh(u_j + u_k - i\lambda) \sinh(u_j - u_k + i2\lambda) \sinh(u_j + u_k + i2\lambda)}. \quad (14)$$

Here  $N$  is the width of the strip (e.g.,  $N = 8$  in Fig. 1) and  $m$  labels the sectors of the transfer matrix, with  $m = N$  for the largest eigenvalue  $\Lambda_0$ . A more convenient sector label is  $\ell = N - m$ .

The Bethe ansatz equations differ from those obtained for case (5a) in the squared prefactor on the left-hand side, which have the cosh functions replaced by sinh. This change is sufficient to alter the finite-size corrections to the eigenvalues and thus the operator content. For case (5a), at the ordinary transition, the Bethe ansatz roots for the largest eigenvalue are uniformly distributed along the real (positive) axis [13]. In contrast, at the special transition we find that the root distribution includes an elementary one-string excitation, located at  $u_1 \sim i(\pi/4 + \lambda/2)$ . To derive the central charge via (7) we thus adopt the analytic method [30], which avoids the explicit manipulation of root densities. Details of the calculations will be presented elsewhere. The bulk free energy  $f_\infty$  is as derived previously [13,17], while the surface free energy  $f_s$  differs from that at the ordinary transition [13]. The result is cumbersome and rather unilluminating in the present context. However, at  $n = 0$ , it reduces to  $f_s = -2 \ln(1 + \sqrt{2})$ . In fact, at this point, we observe that  $\Lambda_0 = (2 + \sqrt{2})^N / (1 + \sqrt{2})^2$  exactly.

For the central charge, we derive the same result,

$$c = 1 - 6(g - 1)^2/g, \quad (15)$$

as for the ordinary transition [10,12,13]. We find that the thermal scaling dimension is associated with an elementary two-string excitation, with

$$X_\epsilon = \frac{2}{g} - 1, \quad (16)$$

in agreement with the conformal invariance result [14]. This result has more recently been obtained from a thermodynamic Bethe ansatz calculation from a conjectured boundary  $S$  matrix [26]. From (11) and (12) the result (16) leads to the crossover exponent  $\phi = \frac{1}{2}$ .

The root distributions for the eigenvalues defining the geometric scaling dimensions are again real, with

$$X_\ell = \frac{1}{4}g(\ell + 1)^2 - \frac{3}{2}(\ell + 1) + \frac{9 - (g - 1)^2}{4g}, \quad (17)$$

where  $\ell = 1, 2, \dots$ . These dimensions are to be compared with those at the ordinary transition, where the result [12,13]

$$X_\ell = \frac{1}{4}g\ell^2 + \frac{1}{2}(g - 1)\ell \quad (18)$$

follows from  $h_{\ell+1,1}$  in the Kac formula [12],

$$h_{p,q} = \frac{1}{4}gp^2 - \frac{1}{2}pq + \frac{q^2 - (g - 1)^2}{4g}. \quad (19)$$

For the adsorption transition, (17) gives

$$X_\ell = \frac{3}{8}\ell(\ell - 2) + \frac{1}{3} \quad (20)$$

at  $n = 0$  ( $g = \frac{3}{2}$ ). The first two values are  $X_1 = -\frac{1}{24}$  and  $X_2 = X_\epsilon = \frac{1}{3}$ , with the exact exponents for the two-dimensional polymer adsorption transition following from (10) and (11). In particular,  $\eta_{\parallel} = -\frac{1}{12}$  and the susceptibility exponent  $\gamma_1 = \frac{93}{64}$ . Guim and Burkhardt [7] originally noted that these were possibly the exact values, as their finite-size scaling estimates for  $X_1$  and  $X_2$  were compatible with  $X_\ell = h_{\ell+1,3}$  in the Kac formula. Indeed we confirm that the more general  $O(n)$  result (17) agrees with  $h_{\ell+1,3}$ . Note that the thermal dimension (16) also belongs to the same family of scaling dimensions, since  $X_\epsilon = h_{1,3}$ . We believe that our results exhaust the complete operator content of the  $O(n)$  model at the special transition.

More recently the  $h_{\ell+1,3}$  result has been conjectured to be correct by Fendley and Saleur [26] who argued that the boundary operator  $\Phi_{\ell+1,3}$  propagates down the strip at the special point. In general, our exact results lend further weight to their claim that the spin degrees of freedom of the Kondo problem can be considered as the  $n = 2$  limit of the special transition of the  $O(n)$  model [26].

So far we have only considered the  $O(n)$  model with boundary conditions that are symmetric with the left and right boundaries of the strip. More generally, it is possible to obtain the Bethe ansatz solutions of the  $O(n)$  model with nonsymmetric boundary conditions by using suitable choices of the reflection matrices. In this way we expect to test recent conformal invariance results for the  $O(n)$  model with mixed boundary conditions [31].

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- [1] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
  - [2] E. Eisenriegler, K. Kremer, and K. Binder, *J. Chem. Phys.* **77**, 6296 (1982).
  - [3] J. M. Hammersley, G. M. Torrie, and S. G. Whittington, *J. Phys. A* **15**, 539 (1982).
  - [4] K. De'Bell and T. Lookman, *Rev. Mod. Phys.* **65**, 87 (1993).
  - [5] K. Binder, in *Phase Transition and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, p. 1.

- [6] R. Vilanove and F. Rondelez, Phys. Rev. Lett. **45**, 1502 (1980).
- [7] I. Guim and T. W. Burkhardt, J. Phys. A **22**, 1131 (1989).
- [8] D. Zhao, T. Lookman, and K. De'Bell, Phys. Rev. A **42**, 4591 (1990).
- [9] H. Meirovitch and I. Chang, Phys. Rev. E **48**, 1960 (1993).
- [10] J. L. Cardy, Nucl. Phys. **B240**, 514 (1984).
- [11] T. W. Burkhardt and J. L. Cardy, J. Phys. A **20**, L233 (1987).
- [12] B. Duplantier and H. Saleur, Phys. Rev. Lett. **57**, 3179 (1986).
- [13] M. T. Batchelor and J. Suzuki, J. Phys. A **26**, L729 (1993).
- [14] T. W. Burkhardt, E. Eisenriegler, and I. Guim, Nucl. Phys. **B316**, 559 (1989).
- [15] E. Domany, D. Mukamel, B. Nienhuis, and A. Schwimmer, Nucl. Phys. **B190**, 279 (1981).
- [16] B. Nienhuis, Phys. Rev. Lett. **49**, 1062 (1982).
- [17] R. J. Baxter, J. Phys. A **19**, 2821 (1986).
- [18] B. Nienhuis, Int. J. Mod. Phys. B **4**, 929 (1990).
- [19] A. G. Izergin and V. E. Korepin, Commun. Math. Phys. **79**, 303 (1981).
- [20] E. K. Skylanin, J. Phys. A **21**, 2375 (1988).
- [21] C. Destri and H. J. de Vega, Nucl. Phys. **B374**, 692 (1992).
- [22] C. M. Yung and M. T. Batchelor, A.N.U. Report No. MRR042-94, hep-th/9410042 (unpublished).
- [23] We note that another orientation of the honeycomb strip geometry can also be treated along the present lines.
- [24] L. Mezincescu and R. I. Nepomechie, Int. J. Mod. Phys. A **7**, 5231 (1991).
- [25] These correspond to reflection matrices for which the corresponding spin chain is not quantum group invariant and thus were seemingly of little interest.
- [26] P. Fendley and H. Saleur, J. Phys. A **27**, L789 (1994).
- [27] H. W. J. Blöte, J. L. Cardy, and M. P. Nightingale, Phys. Rev. Lett. **56**, 742 (1986).
- [28] I. Affleck, Phys. Rev. Lett. **56**, 746 (1986).
- [29] J. L. Cardy, Nucl. Phys. **B270**, 186 (1986).
- [30] See, e.g., S. O. Warnaar, M. T. Batchelor, and B. Nienhuis, J. Phys. A **25**, 3077 (1992); A. Klümper, T. Wehner, and J. Zittartz, J. Phys. A **26**, 2815 (1993), and references therein.
- [31] T. W. Burkhardt and E. Eisenriegler, Nucl. Phys. **B424**, 487 (1994).