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Critical exponents for a self-interacting, directed polymer with adsorption

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We present an exact determination of the correlation-length exponents as well as an accurate numerical estimation of the bulk and surface entropic exponents at the ordinary and special Θ points for a directed-polymer model. The numerical results were obtained using an exact enumeration of walks up to 29 steps.

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Models in which an interacting directed polymer is allowed to absorb to a substrate have been the focus of much attention recently [1–5]. Essentially this has stemmed from the possibility of calculating results analytically for such models and the good quality of numerical results relative to the isotropic case [1]. These studies have been motivated as a way to advance the understanding of dilute solutions of polymers in contact with a substrate, where monomer-monomer interactions result in a collapse transition. The directed-polymer problem appears to contain much of the physics of the isotropic case. It has also been argued that models of this type may correspond to a situation where the polymer chain is subjected to a flow field [6].

Although much is known about the phase diagram for such systems, there are few results on the critical exponents for these problems. In this Brief Report, we present an exact estimation of the correlation-length exponents at the Θ point for the directed polymer, along with a numerical determination, using exact enumeration methods, of the bulk and surface entropic exponents at both the ordinary and special points.

The model which has been most widely studied comprises representing a polymer by a two-dimensional self-avoiding random walk on a square lattice which is directed in that steps in the negative x direction are not allowed [7]. The walk is allowed to gain an energy K for each visit to the adsorbing substrate and an energy J for every pair of nonconsecutive steps which fall in the same row but adjacent columns.

The canonical and grand canonical partition functions can be written

$$Z_L = \sum_{\text{walks length } L} \kappa^l \tau^n , \tag{1}$$

$$\mathcal{Z} = \sum_{\text{walks}} \omega^L \kappa^l \tau^n , \tag{2}$$

where ω is the step fugacity, $\kappa = \exp(K/k_B T)$, and $\tau = \exp(J/k_B T)$. L is the number of monomers in the walk, l the number of visits to the wall, and n the number of monomer-monomer interactions. As before, the procedure is to adjust ω to the critical value required to achieve the thermodynamic limit where

$$\langle L \rangle = \frac{\partial \ln \mathcal{Z}}{\partial \ln \omega} , \tag{3}$$

the average number of monomers, diverges. Quantities of interest are then studied as functions of κ and τ. These include the correlation-length exponents, which may be defined through a characteristic measure of the linear size of the polymer, such as the end-to-end distance or the radius of gyration. Due to the anisotropy of the model presented here, the linear size of the walk scales differently in the x and y directions, defining two exponents

$$\langle \mathcal{R}_x^2 \rangle \sim \langle L \rangle^{2\nu_x} , \tag{4}$$

$$\langle \mathcal{R}_y^2 \rangle \sim \langle L \rangle^{2\nu_y} . \tag{5}$$

The entropic exponents for polymer models may be defined through the canonical partition functions Z_L, Z_L^1, and Z_L^{11} for a polymer in bulk, with one end fixed and both ends fixed to a boundary, respectively. The canonical exponents are then expected to have asymptotic behavior given by

$$Z_L \sim \mu^L L^{\gamma - 1} , \tag{6}$$

$$Z_L^1 \sim \mu^L L^{\gamma_1 - 1} , \tag{7}$$

$$Z_L^{11} \sim \mu^L L^{\gamma_{11} - 1} . \tag{8}$$

The model has the phase diagram shown in Fig. 1 in the (κ, τ) plane with ω adjusted to achieve the thermodynamic limit. For small κ and τ the polymer is unbounded and extended; the number density of visited sites is zero. Increasing κ results in a continuous binding transition to a phase where the fraction of bonds at the substrate is nonzero and the monomer density decays exponentially with the distance from the substrate. Increasing τ the polymer collapses into a phase in which it fills the lattice with a density of visited sites equal to one; the number of unvisited sites is vanishingly small.

The behavior of the directed, self-avoiding walk with $\tau = 1$ was elucidated by Privman, Forgacs, and Frisch [8]. Using transfer matrices in the limit as the width of the system tends to infinity they found that the transition between the extended and adsorbed polymer phases occurs at

$$\omega_\infty = \sqrt{2} - 1 , \tag{9}$$

$$\kappa = \frac{1}{2 - \sqrt{2}} . \tag{10}$$

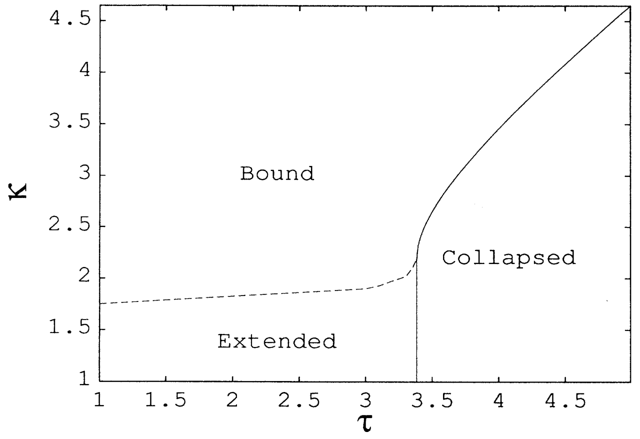

FIG. 1. The phase diagram of a directed polymer in the (κ,τ) plane (after [2]). The dashed line is schematic.

They also found that in the ordinary regime, with $\tau=1$, the entropic exponents are given by $\gamma=1$, $\gamma_1=\frac{1}{2}$, and $\gamma_{11}=-\frac{1}{2}$. Carvalho and Privman [9] also gave the special point values of $\gamma_1=1$ and $\gamma_{11}=\frac{1}{2}$ for a directed polymer at an interface.

The full parameter space was explored numerically by Veal, Yeomans, and Jug [1]. They found the three phases shown in Fig. 1 using transfer matrix techniques in conjunction with finite-size scaling arguments to recover the behavior of the system in the limit of infinite system sizes. They located the multicritical point where the collapsed, extended, and adsorbed phases meet to a high degree of accuracy and gave its location as

$$\omega=0.295\,5977 , \tag{11}$$

$$\kappa=2.191\,488 , \tag{12}$$

$$\tau=3.382\,976 . \tag{13}$$

The location of this multicritical point was subsequently found exactly [2,3], and found to agree with the numerical calculation of Veal, Yeomans, and Jug.

We now turn our attention to the calculation of the correlation-length exponents defined by Eqs. (4) and (5). We consider each of the stable phases in turn.

When the polymer is extended these exponents take the Gaussian values $\nu_x=1$ and $\nu_y=\frac{1}{2}$ [7]. As the polymer collapses it tries to maximize the number of τ bonds while minimizing the number of bonds not involved in nearest-neighbor interactions. In other words the polymer adopts a square geometry. The exponents for a polymer in this configuration are clearly given by $\nu_x=\nu_y=\frac{1}{2}$ if calculated from any suitably defined measure of the size of the polymer. In this phase the end-to-end distance is no longer a suitable measure, since when $\tau\rightarrow\infty$ the value of the end-to-end distance in the y direction depends on how closely the polymer can adopt a square geometry for a given length and does not indicate the overall size of the polymer. These values for the correlation-length exponents are the same as those found for a collapsed isotropic polymer.

It is known that on the phase boundary between the collapsed and extended phases the interacting directed walk may be expressed in terms of two independent noninteracting directed walks living on two sublattices composed of alternate columns of the lattice [2,3]. The combined length of the two subwalks is L', the number of monomers not partaking in monomer-monomer interactions. For clarity, all properties pertaining to the Θ point will be indicated by the superscript Θ. Because the walks on each sublattice behave as if there were no monomer-monomer interactions, the end-to-end distance for a subwalk is given by

$$\mathcal{R}_y^D \propto \langle L' \rangle^{1/2} \tag{14}$$

and

$$\mathcal{R}_x^D \propto \langle L' \rangle , \tag{15}$$

where the superscript D indicates properties specific to the subwalk. Because of the directed nature of the problem it follows immediately that $\mathcal{R}_x^\Theta=2\mathcal{R}_x^D$, that is

$$\langle L' \rangle \sim \langle L \rangle^{\nu_x^\Theta} . \tag{16}$$

If the average distance between the two subwalks is defined as $\mathcal{D}$, it follows by definition that

$$\mathcal{R}_y^\Theta=\mathcal{R}_y^D+\mathcal{D} . \tag{17}$$

The subwalks are made up of the "excess" bonds and are connected by $L-L'$ bonds undergoing nearest-neighbor interactions. Given two subwalk configurations, the distance between them can only be changed by inserting or removing entire rows of interacting monomers. This implies that the average distance between the subwalks is given by

$$\mathcal{D}\sim\frac{\langle L-L' \rangle}{\mathcal{R}_x^\Theta} . \tag{18}$$

Because the subwalks are simple noninteracting directed self-avoiding random walks, the positions of the horizontal bonds on the lattice are uncorrelated within each walk, and because the two walks are independent it is known that they must be uncorrelated between walks. This implies that

$$R_y^\Theta \sim (R_x^\Theta)^{1/2} . \tag{19}$$

The independence of the position of the horizontal bonds also implies that Eq. (18) will apply not only to the subwalks, but any arbitrary subdivision of the excess bonds into two sets, and therefore that $D\sim R_y^\Theta$. From Eqs. (18) and (19), it can then be seen that

$$\frac{\langle L-L' \rangle}{\mathcal{R}_x^\Theta} \sim (R_x^\Theta)^{1/2} . \tag{20}$$

Substituting Eq. (16) into Eq. (20) and rearranging gives

$$L-L^{\nu_x^\Theta} \sim L^{3\nu_x^\Theta/2} . \tag{21}$$

Equation (21) gives $\nu_x^\Theta=\frac{2}{3}$. From Eq. (19) it can then be seen that $\nu_y^\Theta=\frac{1}{3}$. These arguments, and the resulting exponents, also hold at the multicritical point.

Having determined exactly the correlation-length exponents, it is of interest to calculate the entropic exponents. The method adopted here was to use exact enumeration to calculate the canonical partition functions for different L and then use the definitions given in Eqs. (6)–(8) directly. An alternative method also adopted was to use these canonical partition functions as coefficients of a series expansion of the grand canonical partition function and use the methods of differential approximants to calculate the exponents. The exact enumeration was performed in all cases to lengths up to and including $L=29$. The direct calculation approach requires a knowledge of the critical fugacity ω_c at the chosen values of κ and τ, and the series analysis methods are found to work better when this is known.

If $\tau=1$, the entropic exponents are known for the ordinary transition for the solid boundary problem and the special transition for the permeable interface problem. In general the special entropic exponents for the solid boundary problem are not expected to be the same as for the interface problem. The location of the special transition is known to be at $\omega=\sqrt{2}-1$ and $\kappa=1+1/\sqrt{2}$. Using the method of differential approximants gives the values of the surface entropic exponents at this point to be

$$\gamma_1=0.99\pm0.01 , \tag{22}$$

$$\gamma_{11}=0.50\pm0.01 . \tag{23}$$

The location of the collapse transition is also known exactly. An exact enumeration was performed for directed polymers in the bulk at an interface with both ends fixed to the surface and at a solid boundary with one end and both ends on the boundary, respectively. This information is then used in conjunction with the exact location of the ordinary (ord) and special (sp) collapse transitions to calculate all the entropic exponents for a collapsing directed polymer. Results are shown, using both direct calculation and the method of differential approximants, in Table I. It should be noted that the spread of values calculated directly is frequently smaller than the error bars quoted for the results of differential approximants. This is due to oscillations in the coefficients which affect the accuracy of the extrapolation. These oscillations are not of odd-even-type, as in the isotropic model on the square lattice, but display more complicated behavior. While the values calculated directly do not show a monotonic trend, the spread of values decreases with increasing L, and so reasonable error bars are obtained by taking the highest and lowest values obtained. The results would then give values for the entropic exponents as

$$\gamma=0.33\pm0.01 , \tag{24}$$

$$\gamma_{11}^{\text{int}}=-0.04\pm0.07 , \tag{25}$$

$$\gamma_1^{\text{ord}}=-0.33\pm0.02 , \tag{26}$$

$$\gamma_{11}^{\text{ord}}=-1.33\pm0.2 , \tag{27}$$

$$\gamma_1^{\text{sp}}=0.34\pm0.02 , \tag{28}$$

$$\gamma_{11}^{\text{sp}}=0.0\pm0.06 . \tag{29}$$

The superscript int refers to the special exponent for a walk at a permeable interface. γ_1^{int} is trivially the same as γ and has therefore not been quoted separately.

In summary we have calculated exactly the correlation-length exponents for a directed walk model in the presence of an adsorbing substrate at the collapse transition. At this transition we have calculated using exact enumeration techniques the bulk and surface entropic exponents. The results presented here satisfy the scaling relation

$$\gamma+\nu_y=2\gamma_1-\gamma_{11} \tag{30}$$

put forward by Privman, Forgacs, and Frisch for the directed-polymer problem [8]. The exact value for ν_y and the numerical results for the entropic exponents would

TABLE I. Results for the entropic exponents on the boundary between the collapsed and extended phases. The row marked DA presents the results derived using the method of differential approximants.

L	γ	γ_{11}^{int}	γ_1^{ord}	γ_{11}^{ord}	γ_1^{sp}	$\gamma_1^{\text{sp}}-\gamma_{11}^{\text{sp}}$
18	0.325 909	−0.206 765	−0.339 691	−1.461 296	0.342 249	0.310 820
19	0.329 490	−0.147 404	−0.313 286	−1.439 280	0.351 557	0.330 630
20	0.326 747	−0.151 947	−0.330 985	−1.360 901	0.345 943	0.335 674
21	0.331 030	−0.068 547	−0.316 748	−1.221 403	0.325 909	0.322 484
22	0.327 485	−0.154 811	−0.342 318	−1.468 485	0.344 607	0.327 906
23	0.330 926	−0.118 480	−0.332 957	−1.406 544	0.348 178	0.327 955
24	0.331 519	−0.125 317	−0.330 635	−1.362 849	0.349 819	0.327 365
25	0.331 898	−0.071 558	−0.327 414	−1.263 983	0.358 457	0.314 845
26	0.330 757	−0.127 770	−0.343 913	−1.495 956	0.349 786	0.328 764
27	0.332 765	−0.100 052	−0.337 215	−1.432 737	0.351 263	0.332 805
28	0.332 745	−0.112 625	−0.338 668	−1.414 785	0.349 971	0.334 954
29	0.333 078	−0.071 643	−0.336 021	−1.320 541	0.355 062	0.323 969
	γ	$\gamma-\gamma_{11}^{\text{int}}$	γ_1^{ord}	$\gamma_1^{\text{ord}}-\gamma_{11}^{\text{ord}}$	γ_1^{sp}	$\gamma_1^{\text{sp}}-\gamma_{11}^{\text{sp}}$
DA	0.34±0.02	0.38±0.05	−0.37±0.05	1.0±0.2	0.34±0.03	0.34±0.03

seem to indicate possible exact values as [10]

$$\gamma=\tfrac{1}{3}\ , \tag{31}$$

$$\gamma_{11}^{\text{int}}=0\ , \tag{32}$$

$$\gamma_{1}^{\text{ord}}=-\tfrac{1}{3}\ , \tag{33}$$

$$\gamma_{11}^{\text{ord}}=-\tfrac{4}{3}\ , \tag{34}$$

$$\gamma_{1}^{\text{sp}}=\tfrac{1}{3}\ , \tag{35}$$

$$\gamma_{11}^{\text{sp}}=0\ . \tag{36}$$

The tables of coefficients from the exact enumeration are available on request from the author.

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[1] A. R. Veal, J. M. Yeomans, and G. Jug, J. Phys. A **24**, 827 (1991).

[2] D. P. Foster, J. Phys. A **23**, L1135 (1990).

[3] F. Igloi, Phys. Rev. A **43**, 3194 (1991).

[4] D. P. Foster and J. M. Yeomans, Physica A **177**, 443 (1991).

[5] D. P. Foster, J. Stat. Phys. (to be published).

[6] D. J. Klein and W. A. Seitz, in *Nonlinear Topics in Ocean Physics,* Proceedings of the International School of Physics "Enrico Fermi," Course CIX, Varenna, 1991, edited by A. R. Osborne (North-Holland, Amsterdam, 1991).

[7] V. Privman and N. M. Švrakić, *Directed Models of Polymers, Interfaces, and Clusters: Scaling and Finite-Size Properties,* edited by H. Araki, J. Ehlers, K. Hebb, R. Kippenhahn, D. Ruelle, H. A. Weidenmüller, J. Wess, and J. Zittertz, Lecture Notes in Physics Vol. 338 (Springer-Verlag, Berlin, 1989).

[8] V. Privman, G. Forgacs, and H. L. Frisch, Phys. Rev. B **37**, 9897 (1988).

[9] M. C. T. P. Carvalho and V. Privman, J. Phys. A **21**, L1033 (1988).

[10] The γ exponent may be calculated exactly, and is found to be $\frac{1}{3}$ [A. Owczarek (private communication)].