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LETTER TO THE EDITOR

Adsorption of directed polymers

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Abstract. We calculate the phase diagram of a directed polymer with nearest-neighbour interactions on a semi-infinite square lattice with an attractive wall. The calculations are performed by numerically diagonalising the transfer matrix on strips of width N and extrapolating to $N = \infty$.

Polymer adsorption on a substrate has received considerable attention both because of its intrinsic merit as an interesting problem in statistical mechanics [1] and because of its technological importance in the stabilisation of colloidal dispersions used in paints, pharmaceuticals and foodstuffs [2]. The adsorption of a self-avoiding walk is now well understood as a multicritical point with associated scaling laws [3]. The critical exponents can be predicted exactly in two dimensions using conformal invariance [4-6]. However, there has been much less work in the case where the surface attraction competes with monomer-monomer interactions. The only calculation of a phase diagram for such a system that we are aware of is by Bouchaud and Vannimenus [7] who use a real-space renormalisation group approach.

Therefore, in this letter we calculate the phase diagram of a directed self-avoiding walk with nearest-neighbour attractive interactions in the presence of an absorbing wall. This situation is of interest particularly when adsorption takes place in the presence of shear flow parallel to the surface. The calculations are performed by numerically diagonalising the transfer matrix on strips of width N and then extrapolating to $N = \infty$. The finite-size behaviour is very regular and gives us considerable confidence in the accuracy of the phase diagram.

We consider a directed polymer on a strip of width N as shown in figure 1. The polymer is directed in that steps in the negative x direction are forbidden. Hence, the position of the polymer in column i , n_i , is unique. The attraction to the substrate is modelled by assigning an energy K to each column in which $n_i = 1$ or N . Nearest-neighbour interactions between monomers are introduced through an attractive energy J between bonds which occupy the same row in adjacent columns.

The generating function of this model can be written

$$\mathcal{Z} = \sum_{\text{walks}} \omega^L \kappa^I \tau^n \quad (1)$$

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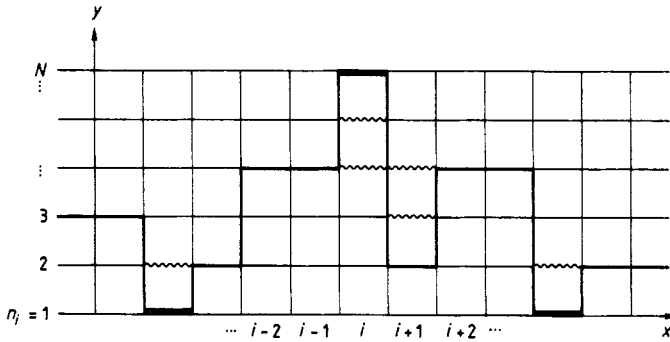


Figure 1. A directed polymer on a strip of width N . The polymer interacts with the surface of the strip (double lines). Monomer-monomer interactions are represented by wavy lines.

where ω is the monomer fugacity, $\kappa = e^{-K/k_B T}$, $\tau = e^{-J/k_B T}$, L counts the total number of monomers, l the number of monomers lying in a surface and n the number of nearest-neighbour interactions.

To calculate \mathcal{Z} we follow Privman and Švrakić [8] and write (1) in terms of a transfer matrix, \mathbf{T} . The transfer matrix elements, $T_{\alpha\beta}$, are labelled by the values of $\alpha = (n_i, n_{i+1})$ and $\beta = (n_{i+1}, n_{i+2})$ and are defined by

$$T_{\alpha\beta} = \omega^{L_{\alpha\beta}} \kappa^{l_{\alpha\beta}} \tau^{n_{\alpha\beta}} \quad (2)$$

where

$$L_{\alpha\beta} = 1 + (|n_i - n_{i+1}| + |n_{i+1} - n_{i+2}|)/2 \quad (3)$$

$$l_{\alpha\beta} = \delta_{n_{i+1}, 1} + \delta_{n_{i+1}, N} \quad (4)$$

$$n_{\alpha\beta} = \min(|n_i - n_{i+1}|, |n_{i+1} - n_{i+2}|). \quad (5)$$

The sum of the Boltzmann weights of all walks with L_x steps in the x direction is

$$\mathcal{Z}_{L_x} = \mathbf{v}^T \mathbf{T}^{L_x} \mathbf{u} \quad (6)$$

where \mathbf{v} and \mathbf{u} are vectors depending on the initial and final positions of the polymer. Summing over L_x gives the generating function for all walks on the lattice,

$$\mathcal{Z} = \sum_{L_x} \mathcal{Z}_{L_x} = \mathbf{v}^T \mathbf{T} (\mathbf{1} - \mathbf{T})^{-1} \mathbf{u}. \quad (7)$$

It can be seen immediately from (7) that the singularity in \mathcal{Z} corresponding to the critical fugacity, ω^* , occurs when the largest eigenvalue of the transfer matrix, λ^{\max} , is unity.

We have obtained finite-size approximations to the critical fugacity, ω_N^* , by calculating the largest eigenvalue of the transfer matrix for a strip of width N , λ_N^{\max} , and putting it equal to one. The finite-size results behave in a very regular way and give rather firm evidence for the phase diagram shown in figure 2. We shall now describe in more detail how this phase diagram was obtained.

We begin with the adsorption transition. The finite-size critical fugacity, $\omega_N^*(\kappa)$, is shown for different values of τ in figure 3.

Consider first the case of no monomer-monomer interactions, $\tau = 1$. For the semi-infinite system this limit has been solved exactly by Privman *et al* [8, 9] who found an adsorption transition at $\omega^* = \sqrt{2} - 1$, $\kappa^* = 1 + 1/\sqrt{2}$. Their analysis can be

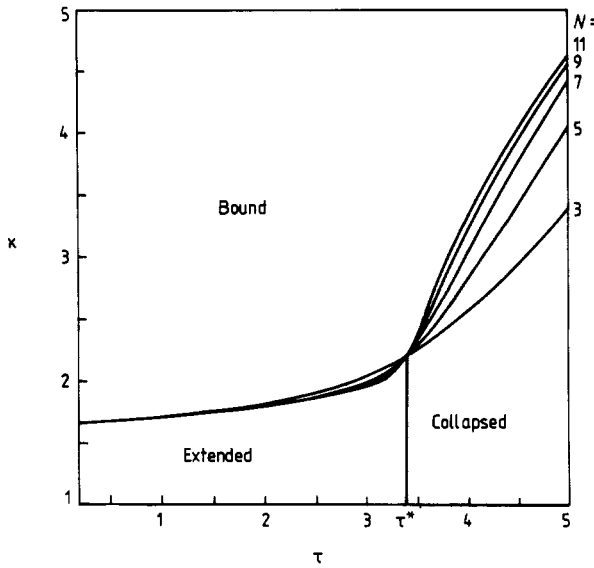


Figure 2. Phase diagram of the directed polymer showing the extended, collapsed and bound phases. Successive approximations to the adsorption phase boundary, $\kappa_N^*(\tau)$, were obtained from (13, 14) for $N = 3, 5, \dots, 11$.

extended to finite N , using methods similar to those employed in related models of interfacial wetting [8, 10]. The results provide a useful check on the numerical calculations and indicate their asymptotic convergence with increasing N . In the extended phase, $\kappa < \kappa^*$,

$$\omega_N^* - \omega^* = \frac{\pi^2}{4(N-1)^2} + O\left[\frac{1}{(N-1)^3}\right] \tag{8}$$

whereas in the bound phase we find the expected exponential dependence of the leading correction term on N . Near the adsorption transition, (ω^*, κ^*) , the phase boundary can be written in terms of the scaled variables

$$u = N|\omega^* - \omega|^{1/2} \tag{9}$$

$$v = N|\kappa^* - \kappa| \tag{10}$$

as

$$v = (1 + \sqrt{2})u \tanh u \quad \kappa \geq \kappa^*, v \ll 1 \tag{11}$$

$$v = (1 + \sqrt{2})u \tan u \quad \kappa \leq \kappa^*, v \ll 1. \tag{12}$$

Hence, for $\tau = 1$, the critical curves cross at (ω^*, κ^*) for all values of N .

For $\tau \geq 1$, a sequence of finite-size approximations to the position of the adsorption transition, (ω_N^*, κ_N^*) , were obtained from the crossing points of curves for strips of width N and $N+2$:

$$\lambda_N^{\max}(\omega_N^*, \kappa_N^*) = 1 \tag{13}$$

$$\lambda_{N+2}^{\max}(\omega_N^*, \kappa_N^*) = 1. \tag{14}$$

The resulting variation of κ_N^* with τ for $N = 3, 5, \dots, 11$ is shown on the phase diagram in figure 2.

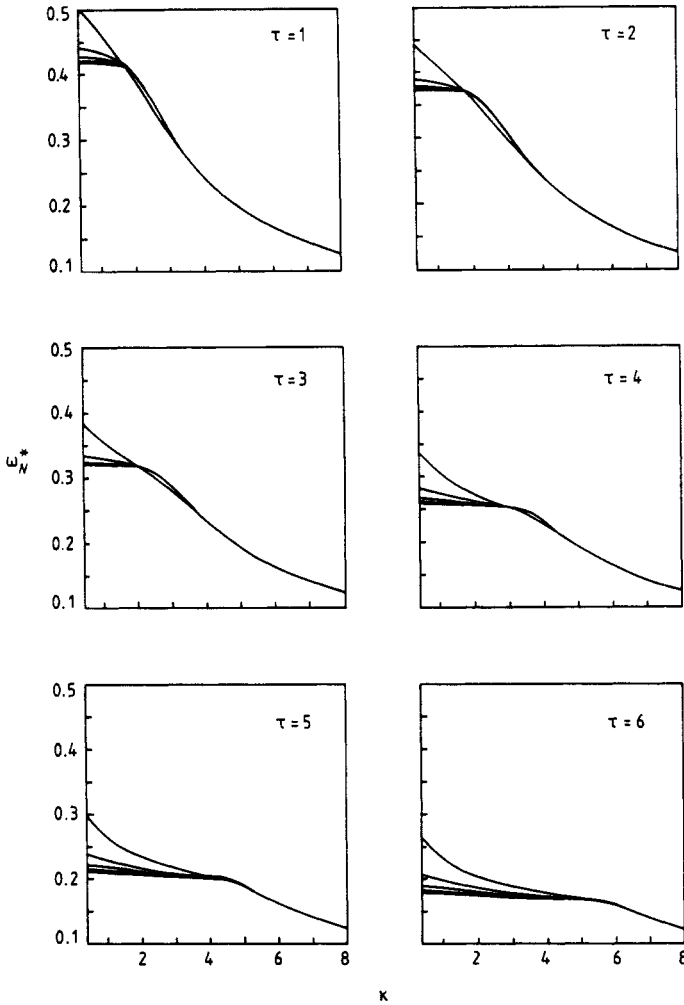


Figure 3. Dependence of the critical fugacity on surface binding potential, $\omega_N^*(\kappa)$ for $N=5, 9, \dots, 21$ for values of τ between 1 and 6. The intersection point of curves is κ_N^* .

The curves in figure 3 retain the same general appearance as τ increases. In the bound phase, the convergence to ω^* is exponentially fast and therefore the results show little dependence on N , except in the vicinity of the adsorption transition. Above the adsorption transition, $\kappa < \kappa^*$, ω_N^* converges approximately as

$$\omega_N^* - \omega^* \sim (N-1)^{-\alpha_{\text{eff}}} \quad (15)$$

where the effective exponent α_{eff} varies from 2 at $\tau=1$ to 1 for large τ . The crossover is associated with the transition from the extended phase to the collapsed phase.

It is also instructive to look at the fraction of adsorbed monomers, defined as the ratio of the average number of bonds at the surface, $\langle I \rangle$, to the average number of bonds, $\langle L \rangle$, where the averages are evaluated at the critical fugacity. This quantity is an order parameter for the adsorption transition. Finite-size data as a function of κ for different values of τ are shown in figure 4. They show clear evidence for a transition at κ^* . Note, however, that the character of the transition appears to change with

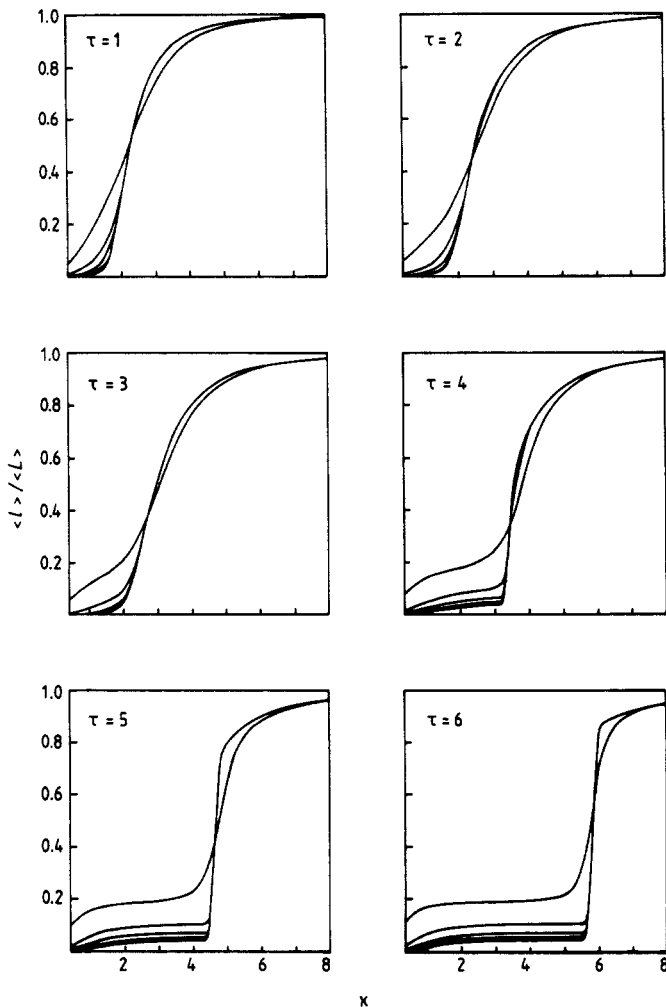


Figure 4. The fraction of adsorbed monomers at the critical fugacity, ω_N^* , plotted as a function of binding potential, κ , for values of τ between 1 and 6.

increasing τ . It is tempting to identify the adsorption transition of the extended polymer as second order and that of the collapsed polymer as first order.

To see if this is a reasonable premise and to complete the phase diagram we now consider the collapse transition itself. Figure 5(a) shows extrapolated values of the product $\tau\omega^*$ for $\kappa = 1$ (no surface interaction) as a function of τ . The extrapolated values were estimated assuming an effective power law convergence (15) and determining the effective exponent from a triplet of consecutive finite-size estimates [11]. Figure 5(b) shows finite-size data for the average number of interactions per monomer at the critical fugacity, $\langle n \rangle / \langle L \rangle$, as a function of τ for $\kappa = 1$. Both graphs indicate a phase transition at $\tau^* \approx 3.4$. One would expect this value to be independent of κ and very similar data to those presented in figure 5 have been obtained for $\kappa = 1.5$ and 2.

Returning to figure 2, the curves $\kappa_N^*(\tau)$ cross at a point

$$(\tau^*, \kappa^*) = (3.382\,976, 2.191\,488) \tag{16}$$

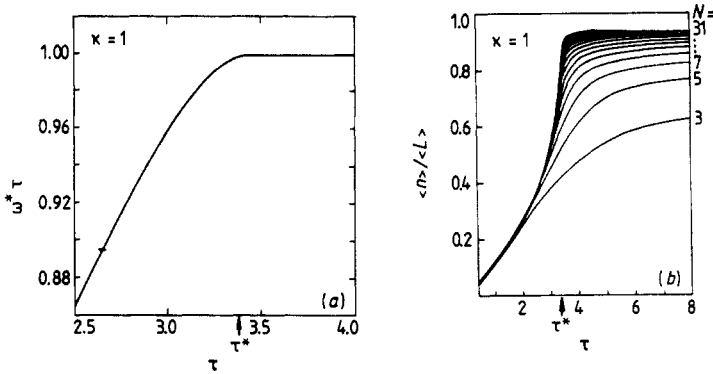


Figure 5. The variation of (a) extrapolated values of the product $\tau\omega_N^*$, and (b) the average number of interactions per monomer at the critical fugacity, with τ for $\kappa = 1$. The transition is expected to occur at $\tau^* = 3.383$ (shown by an arrow in the figures): this correspond to the value of τ at the multicritical point.

(for which $\omega^* = 0.295\,5977$) independent of N and it is tempting to identify this as the position of the multicritical point. If this is the correct identification, the independence of the size of the system suggests that this is an exact result to numerical precision. Because the position of the collapse transition is expected to be independent of κ above the adsorption transition, in a semi-infinite system, we conclude that $\tau^* = 3.382\,976$ for all $\kappa < \kappa^*$, in agreement with the results shown in figure 5. For $d > 2$, a bound-extended/bound-collapsed transition line should also exist for $\kappa > \kappa^*$.

To conclude, we have calculated the phase diagram of a directed polymer with an adsorbing wall and monomer-monomer interactions using finite-size scaling. Accurate results are possible even with small strip widths. The transfer matrix has dimension N^2 , with N^3 non-zero elements. It is not difficult to go to higher values of N and we have obtained results for N up to 51 which confirm the picture presented here. The numerical results provide strong evidence that the adsorption transition is second order when the unbound polymer is extended but first order when it is collapsed. We identify the multicritical point where the collapse and adsorption transitions coincide as the point where the curves $\kappa_N^*(\tau)$ cross. This point appears numerically to be independent of N and hence, if the identification is correct, the result is exact. Our phase diagram agrees qualitatively with that of Bouchaud and Vannimenus [7] who performed a real-space renormalisation group calculation for the three-dimensional Sierpinski gasket.

A problem of great interest is the collapse-adsorption multicritical behaviour of isotropic self-avoiding walks in two dimensions. This is more difficult because of the larger sizes of the transfer matrices [12] and because the allowed configurations of the collapsed polymer that can fit on the strip depend strongly on N . However, the results presented here have proved a useful guide to the most efficient method of analysis for that problem. Results for the isotropic model and more details of the work described in this letter will be presented elsewhere.

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