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LETTER TO THE EDITOR

**Adsorption of a directed polymer chain in the presence of monomer attraction: analytical results**

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**Abstract.** The adsorption of a directed polymer chain is studied in two dimensions using a restricted solid-on-solid model and allowing for a short range attraction between monomers. All the thermodynamic properties of the chain are evaluated exactly. The system does not exhibit a collapse or chain folding transition.

In a series of recent papers [1-4] the question of the adsorption of a single directed polymer chain was studied in two dimensions,  $d = 2$ . The chain was modelled by a solid-on-solid model used earlier by Privman *et al* [5] complemented by an additional energy term describing the attraction between monomers. In [1] it was argued on the basis of numerical results that, in addition to the adsorption-desorption transition found in [5], for a sufficiently strong monomer attraction a first-order chain-folding or collapse transition also takes place. In [2-4] additional analytical results were derived for the phase diagram.

The chain-folding transition was studied a long time ago by Zwanzig and Lauritzen [6]. These authors derived an exact expression for the grand canonical partition function of the chain in 2D, described by a model similar to the sos model. On the basis of their exact result they concluded that the chain-folding transition was second order. At the transition the specific heat exponent  $\alpha = \frac{1}{2}$ . It has to be noted that the result of [1-4] concerning the order of the transition is still based on numerical evidence.

In the present work we report results obtained for the above problem, using a restricted sos (rsos) model for the description of the polymer chain. The advantage of the rsos model is that all the calculations can be performed exactly. However, imposing the restriction on the sos model washes out the collapse transition. In the earlier studies of interfaces by means of solid-on-solid-like models, one got used to the fact that sos and rsos models basically give the same results, especially if universal properties are studied [7]. In the present situation this is not the case. Although the rsos version of polymer adsorption in the presence of monomer-monomer interaction is less spectacular, due to the availability of exact analytical expressions for all thermodynamic quantities, a number of interesting conclusions can be made, as well as enabling some of the earlier results to be better understood.

Consider a directed random walk on a two-dimensional square lattice shown in figure 1. The left end of the chain is grafted to the surface at  $n = 0$ . In terms of the higher valued  $n_i$  height variables the sos model of this chain can be modelled by the transfer matrix  $T$  with matrix elements (see [11])

$$T_{\alpha\beta} = \omega^{L_{\alpha\beta}-1} \kappa^{l_{\alpha\beta}} \tau^{M_{\alpha\beta}}. \quad (1)$$

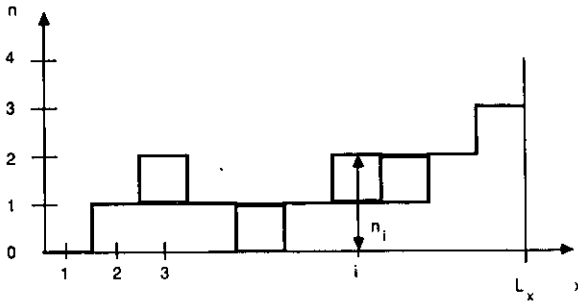


Figure 1. A typical configuration of a directed polymer chain described by a RSOS model. Heavy lines of unit length stand for monomers and the double lines denote possible interactions between monomers.

Here  $\alpha = (n_i, n_{i+1})$ ,  $\beta = (n_{i+1}, n_{i+2})$ ,  $\omega$  is the fugacity,  $\kappa$  and  $\tau$  are respectively the Boltzmann weights due to the surface attraction and the monomer-monomer attraction and are given by  $\kappa = e^{K/kT}$ ,  $\tau = e^{J/kT}$  with  $K, J > 0$ . For  $L, l$  and  $M$  in (1) one has

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

$$l_{\alpha\beta} = \delta_{n_{i+1}, 0} \quad (3)$$

$$M_{\alpha\beta} = \min(|n_i - n_{i+1}|, |n_{i+1} - n_{i+2}|) \frac{1}{2} \{1 - \text{sign}[(n_i - n_{i+1})(n_{i+1} - n_{i+2})]\}. \quad (4)$$

The grand partition function of the chain can be written as

$$\mathcal{Z} = \sum_{L_x} Z_{L_x} = \langle v | \omega T (1 - \omega T)^{-1} | u \rangle. \quad (5)$$

Here  $Z_{L_x}$  is the Boltzmann weight of all walks with  $L_x$  steps in the  $x$  direction, and  $v, u$  are vectors determining respectively the initial and final positions of the chain (since we graft the left end of the chain,  $\langle v | = \langle 0 |$ ). In the earlier studies [1-4] the differences  $|n_i - n_{i+1}|$  could take on any value. We now restrict this difference to take on only the values 0 and 1, and consider the following ansatz for the eigenvector of  $T$  corresponding to the largest eigenvalue.

$$\phi_{nn'} = \begin{cases} b_0 & \text{for } n = n' = 0 \\ \sqrt{\omega} b_1 e^{-\mu} & \text{for } n = 0, n' = 1 \\ \sqrt{\omega} a_{(n-n')} e^{-n'\mu} & \text{for } n \geq 1. \end{cases} \quad (6)$$

With  $\mu > 0$  the above eigenvector could in principle describe the adsorbed state of the chain. Inserting the above ansatz into the eigenvalue equation for  $T$ , and fixing the normalization of  $\phi$  by putting  $a_0 = 1$ , it follows that  $b_1 = a_{-1}$ . Denoting the largest eigenvalue by  $\lambda$ , one obtains the following system of equations for the five unknowns  $b_0, a_{-1}, a_1, \mu, \lambda$ :

$$\kappa b_0 + \kappa \omega a_{-1} e^{-\mu} = \lambda b_0 \quad (7)$$

$$\kappa b_0 + \kappa \omega \tau a_{-1} e^{-\mu} = \lambda a_1 \quad (8)$$

$$\omega a_1 e^{\mu} + 1 + \omega \tau a_{-1} e^{-\mu} = \lambda a_1 \quad (9)$$

$$\omega a_1 e^{\mu} + 1 + \omega a_{-1} e^{-\mu} = \lambda \quad (10)$$

$$\omega \tau a_1 e^{\mu} + 1 + \omega a_{-1} e^{-\mu} = \lambda a_{-1}. \quad (11)$$

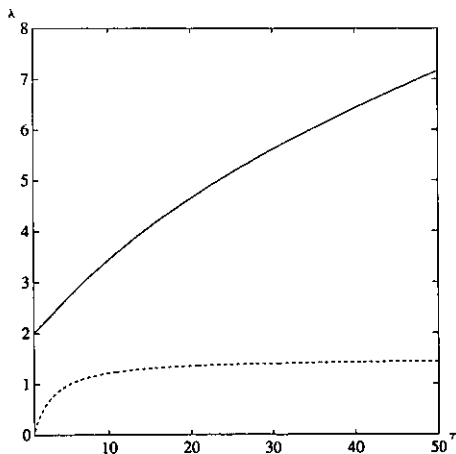
From the last three equations one can express  $\lambda$  as a function of  $\omega$ ,  $\tau$  and  $\mu$ . This leads to the following third-order equation

$$\lambda^3 - \lambda^2(1 + 2\omega \cosh \mu) - \lambda\omega^2(\tau^2 - 1) + \omega^2(\tau - 1)^2 = 0. \quad (12)$$

It can be seen from the above equation that the adsorption-desorption transition of the chain cannot be first order, no matter what the values of  $\omega$  and  $\tau$  are. At the unbinding transition  $\mu$  becomes zero, and hence in the unbound state  $\lambda$  is independent of  $\mu$ . The deviation from the transition can be characterized in terms of  $\mu$ . Since from (12) it follows that  $\lambda$  is an even function of  $\mu$ , one concludes that all the first derivatives of  $\lambda$  with respect to  $\mu$  are continuous at the transition.

Once the largest eigenvalue of  $T$  is known, the thermodynamic properties of the chain can be easily obtained in the limit when the average length of the chain  $\langle L \rangle \rightarrow \infty$ . This corresponds to a singularity which develops in the denominator in (5). The infinite chain limit is then defined by  $\omega\lambda = 1$ . Using this relationship and  $\mu = 0$  in (12) one obtains for the two physically acceptable values of  $\lambda$  as a function of  $\tau$  the result shown in figure 2. A first-order transition could be obtained if the two curves in figure 2 intersected. However, in the RSOS model this never happens. Using (7) and (8) one can obtain the phase diagram analogous to the one shown in figure 2 in [1]. This is shown in figure 3, whereas the density of the interacting monomers (which quantifies the extent of chain folding),  $\langle M \rangle / \langle L \rangle$  in the infinite chain limit is shown in figure 4. Figure 4 shows the continuous variation of this density across the phase boundary of figure 3. Comparing the derived phase diagram with that of [1], one remarks that not only is the line of first-order transitions from the collapsed to the extended state missing, but the  $\kappa = \kappa(\tau)$  curve is qualitatively different from the one given in [1-4]. This can be understood from the following analysis.

Let us consider the  $\tau \rightarrow \infty$  limit in both the SOS and the RSOS models. It can be easily shown that for a chain of length  $L$ , for large  $L$  the monomer-monomer interaction term is maximized in the SOS model when the chain acquires the shape shown in figure 5. (We assume a finite  $\kappa$ .) It consists of columns with  $n \sim \sqrt{L}$  and there are  $\sim \sqrt{L}$  such columns. Fluctuations around the shape shown in figure 5 are still present. In this limit  $\langle M \rangle / \langle L \rangle \rightarrow 1$ . The picture is entirely different in the RSOS model, as can be seen



**Figure 2.** The two physically allowed solutions of equation (12) for the maximal eigenvalue of the transfer matrix as a function of  $\tau$ . A first-order transition could take place if the two curves intersected.

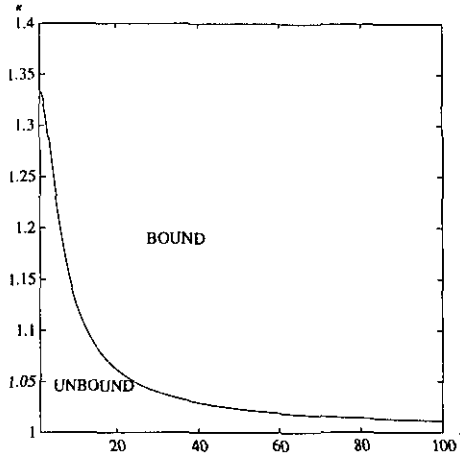


Figure 3. The phase diagram of the adsorption-desorption transition in the presence of monomer attraction in terms of  $\kappa$  and  $\tau$ .

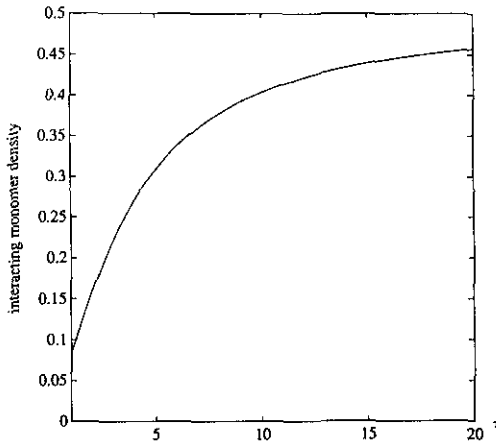


Figure 4. The interacting monomer density as a function of  $\tau$  along the phase boundary depicted in figure 3.

from figure 6. In the  $\tau \rightarrow \infty$  the chain becomes rigid and a tremendous loss of entropy takes place relative to the situation in the sos model. In the limit of infinite chain  $\langle L \rangle = 2\langle L_x \rangle$  and  $\langle M \rangle = \langle L_x \rangle$ , which is the asymptotic value that the curve in figure 4 reaches. Since  $\langle M \rangle / \langle L \rangle \rightarrow 1$  in the sos model, and there are only  $\sim \sqrt{L}$  monomers attracted to the surface, in order to keep the chain bound to the surface the critical value of  $\kappa$  must tend to infinity with  $\tau \rightarrow \infty$ . One obtains the phase diagram shown for example in figure 2 in [1]. In the rsos model, where  $\langle M \rangle = \langle L_x \rangle$  and since (as can be seen from figure 6) the number of monomers attached to the surface is also  $\langle L_x \rangle$ , an infinitesimal  $\kappa$  already keeps the chain bound to the surface. Hence, one obtains the phase diagram shown in figure 3.

Another interesting way to compare the sos and rsos models is to recall the way the authors in [2-4] 'derived exactly' part of the phase diagram. It was argued that in the collapsed phase, where  $\langle M \rangle / \langle L \rangle \neq 0$  the product  $\omega\tau$  acts as an effective fugacity, and therefore  $\mathcal{Z}$  must develop a singularity at  $\omega\tau = 1$ . The location of the multicritical

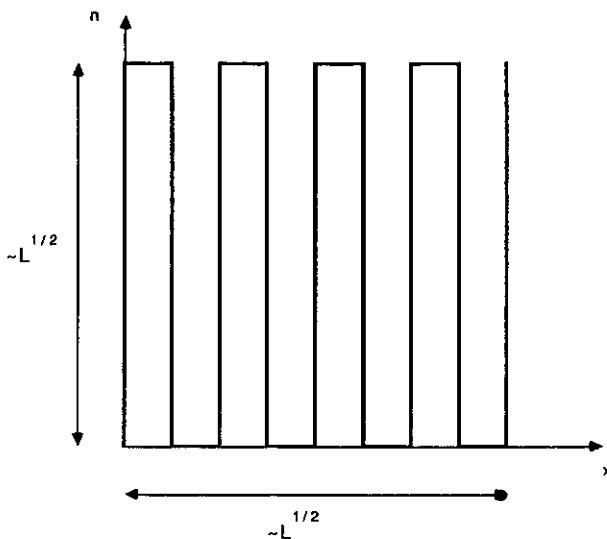


Figure 5. The configuration of a directed polymer chain modelled by a SOS model in the limit of infinitely strong monomer interaction.

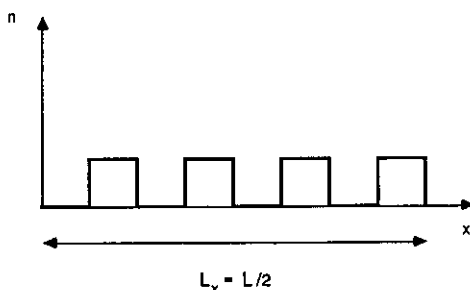


Figure 6. The configuration of a directed polymer chain modelled by a RSOS model in the limit of infinitely strong monomer interaction.

point, where the adsorption-desorption transition turns from second order to first order was obtained from the intersection of the curve  $\omega = 1/\tau$  and the curve which gives the phase boundary between the bound and extended phases expressed in terms of  $\omega$  and  $\tau$  (instead of  $\kappa$  and  $\tau$  as is done in figure 3). In the RSOS model the condition  $\omega\tau = 1$  should be replaced by  $\omega\sqrt{\tau} = 1$ , since here  $\langle M \rangle / \langle L \rangle = \frac{1}{2}$  in the infinite chain limit, when  $\tau \rightarrow \infty$ . Figure 7 shows the two curves in the RSOS model. Instead of crossing, these two curves smoothly join each other because both of them behave as  $\omega = 1/\sqrt{\tau}$  for large values of  $\tau$ .

In conclusion, we presented the exact solution of a RSOS model in  $d = 2$  describing the adsorption-desorption transition of a directed polymer chain in the presence of monomer-monomer interaction. Contrary to the results obtained within the SOS treatment of the same problem we do not find a collapse transition.

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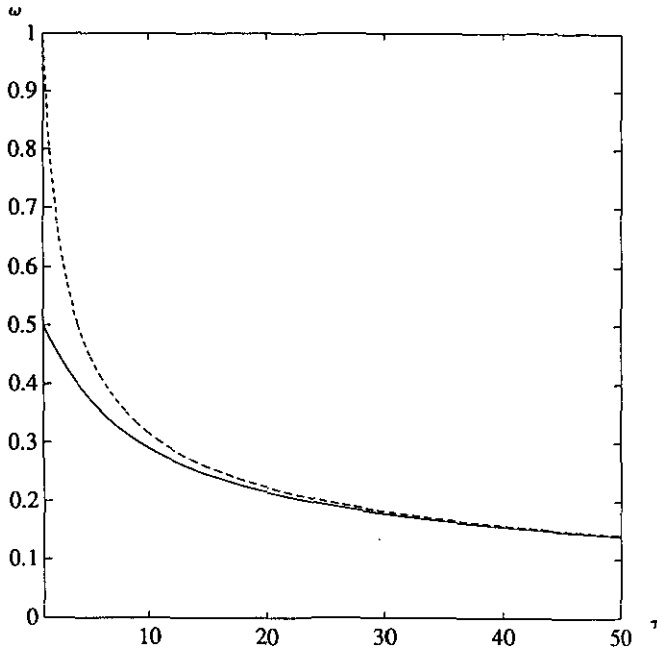


Figure 7. The broken curve is  $\omega = 1/\sqrt{\tau}$ , the full curve is the phase boundary between the bound and unbound regions (the same as in figure 3) in terms of  $\omega$  and  $\tau$ .

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