

Tension of polymers in a strip

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Abstract. We consider polymers, modelled as self-avoiding chains, confined on a strip defined on the square lattice with spacing a in the (x, y) plane, limited by two walls which are impenetrable to the chains and located at $x = 0$ and $x = am$. The activity of a monomer incorporated into the chain is defined as $z = \exp(\beta\mu)$ and each monomer adsorbed on the wall, that is, located at sites with $x = 0$ or $x = m$, contributes with a Boltzmann factor $\omega = \exp(-\beta\epsilon)$ to the partition function. Therefore, $\epsilon < 0$ corresponds to walls which are attractive to the monomers, while for $\epsilon > 0$ the walls are repulsive. In particular, we calculate the tension between the walls, as a function of m and ω , for the critical activity z_c , at which the mean number of monomers diverges (the so called polymerization transition). For $\omega > 1 \rightarrow 1.549375\dots$, the tension on the walls is repulsive for small values of m , becoming attractive as m is increased and finally becoming repulsive again. As ω is increased, the region of values of m for which the tension is attractive grows.

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1 Introduction and definition of the model

Dilute polymers in good solutions have been modelled for quite a long time by self-avoiding chains on regular lattices [1]. The much more treatable model of *ideal* chains, where there are no excluded volume interactions and thus the self-avoidance constraint is relaxed, has also been considered for studying properties of polymers, but it has been recognized that many properties of the model, in particular the critical ones, are strongly dependent of the self-avoidance constraint. The behavior of these models in restricted geometries, where the chains are confined to regions of the lattice limited by walls, wedges or slabs, was considered more recently, both through rigorous [2] and finite size scaling methods [3].

The model we are studying here is of chains confined to a one-dimensional strip defined on a square lattice in the (x, y) plane. If we denote the lattice parameter by a , the strip of width ma is limited by walls placed at $x = 0$ and $x = ma$, $m = 0, 1, 2, \dots$. The activity of a site of the lattice incorporated into the chain (monomers) will be denoted by $z = \exp(\beta\mu)$ and a short range interaction between the monomers and the walls will be included, associating an energy ϵ to every monomer located at $x = 0$ or $x = ma$. Thus the walls are attractive if $\epsilon < 0$ and repulsive if $\epsilon > 0$. This model may be used to study the problem of polymers confined between two plates, which is relevant for the properties of stabilization of colloidal suspensions by

polymers, the growth of lamellar polymeric crystals from the bulk phase, and the use of polymers as an adhesive between plates [4]. It should be stressed, however, that most of the applications are in three dimensions, and our results are valid on a strip defined on the square lattice. Experimental studies of polymers confined on surfaces have been done, however, one possibility being the use of chains with properties such that they are restricted to the surface of a solvent or to the interface of two immiscible liquids [5]. Polymer models may display qualitatively different behavior in two and three dimensions [6]. The model defined above has been studied thoroughly for *ideal* chains, where the chain configurations considered correspond to random walks on the lattice [4], but it would be interesting to study the effects of the excluded volume interactions on its thermodynamical properties. In a previous work [7], we found that the density profile of the monomers inside the strip changes qualitatively when the self-avoidance constraint is introduced. Here we will consider the tension between the walls.

The appropriate partition function for the model defined above is

$$G = \sum z^N \omega^{N_w}, \quad (1)$$

where the sum is over *all* chains with suitable boundary conditions defined below, N is the number of monomers in the chain, N_w of them being placed on the walls ($x = 0, ma$). The Boltzmann factor associated to a monomer

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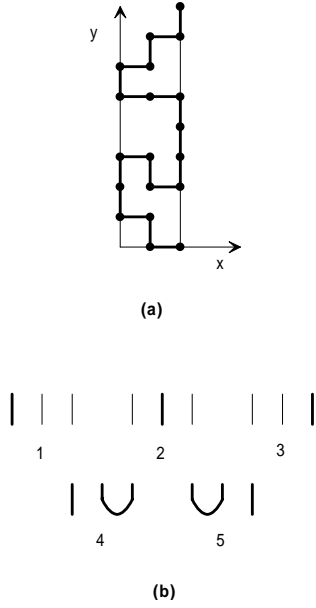


Fig. 1. (a) A walk for $m = 2$, with 19 monomers. The statistical weight of this walk is equal to $z^{19}\omega^{12}$. (b) The five possible line configurations for $m = 2$. Configurations 3 and 5 may be obtained from configurations 1 and 4 by reflection operations, respectively.

located on the walls is

$$\omega = \exp(-\beta\epsilon). \quad (2)$$

A chain contributing to the sum and its statistical weight may be seen in Figure 1. In order to calculate the partition function above, we will use a combination of the generating function method, which was much used in the study of *directed* polymers [8], with the transfer matrix formalism [9], to ensure that the self-avoidance constraint is properly taken into account. Therefore, we define a line configuration by specifying the connectivity properties of a chain arriving at a particular line y through paths which pass only through sites of the lattice situated below, that is, with smaller values of y . It is sufficient to specify the bond which is linked to the initial monomer of the chain and the pairs of bonds linked together. In Figure 1 the five possible line configurations for $m = 2$ are shown. The number of line configurations will be called $n_c(m)$ and increases rapidly with m . We then define $n_c(m)$ partial partition functions of the chains arriving at line y from below with line configuration k

$$g_y(k) = \sum' z^{N(y,k)} \omega^{N_w(y,k)}, \quad (3)$$

where the prime denotes that the sum is restricted to chains with no bond at or above y and whose line configuration arriving at y is labeled by k . Only contributions of monomers placed below line y are included in equation (3). One may then consider the set of chains with one more step in the y direction and find that its partial

partition functions are related to $g_y(k)$ through linear recursion relations:

$$g_{y+a}(i) = \sum_{j=1}^{n_c(m)} A(i,j) g_y(j). \quad (4)$$

The elements of the transfer matrix A are monomials in z and ω , corresponding to the contributions of monomers placed on line y . In the cases where the line configuration j may not be followed by the line configuration i , the matrix element $A(i,j)$ is set equal to zero. We show this matrix for $m = 2$ as an example

$$A = \begin{pmatrix} \omega z & \omega z^2 & \omega^2 z^3 & \omega^2 z^3 & 0 \\ \omega z^2 & z & \omega z^2 & 0 & 0 \\ \omega^2 z^3 & \omega z^2 & \omega z & 0 & \omega^2 z^3 \\ 0 & 0 & \omega^2 z^3 & \omega^2 z^3 & 0 \\ \omega^2 z^3 & 0 & 0 & 0 & \omega^2 z^3 \end{pmatrix}. \quad (5)$$

Since we have vanishing elements in the transfer matrix, the model may display phase transitions. These polymerization transitions for one-dimensional models are of first order [10,11].

We define the initial condition on the chains by placing the starting monomer at line $y = 0$, thus the initial partial partition functions are

$$g_0(k) = \sum_{i=1}^{m+1} \delta_{k,i}, \quad (6)$$

where we make the convention that the first $m + 1$ line configurations have only one bond of the chain coming from below. If we now consider the ensemble of all walks ending at any line $y > 0$ with line configuration k , the appropriate partition functions will be

$$G(k) = \sum_{i=1}^{\infty} g_{ia}(k). \quad (7)$$

Considering the recursion relations, equation (4), we find that the partition functions $G(k)$ satisfy a set of $n_c(m)$ linear equations

$$\sum_{j=1}^{n_c(m)} [A(i,j) - \delta_{i,j}] G(j) = -g_0(i). \quad (8)$$

The solution of this set of equations may be written as a ratio of two determinants

$$G(i) = \frac{|B_i|}{|A - I|}, \quad (9)$$

where I is the identity matrix and B_i are matrices obtained replacing the i th column of $A - I$ by vector $-\mathbf{g}_0$. Finally, we may choose a final condition on the walks considered restricting the final line configuration to be one of the first $m + 1$, thus the partition function will be

$$G = \sum_{i=1}^{m+1} G(i). \quad (10)$$

If we define the thermodynamic potential

$$\Psi = \frac{-\ln(G)}{\beta}, \quad (11)$$

we may calculate the mean value of the number of monomers

$$\langle N \rangle = -\frac{\partial \Psi}{\partial \mu} = \frac{z}{G} \frac{\partial G}{\partial z}, \quad (12)$$

as well as the tension acting on the walls

$$F = \frac{1}{a} \left(\frac{\partial \Psi}{\partial m} \right)_{z,\omega}, \quad (13)$$

where the tension is positive if it is attractive.

Considering expressions (9, 10) for the partition function G , the mean number of monomers will be

$$\langle N \rangle = z \left(\frac{1}{\sum_{i=1}^{m+1} |B_i|} \frac{\partial \sum_{i=1}^{m+1} |B_i|}{\partial z} - \frac{1}{|A-I|} \frac{\partial |A-I|}{\partial z} \right). \quad (14)$$

We notice that $\langle N \rangle$ diverges as $|A-I| \rightarrow 0$, and this is the critical condition. It should be stressed that, although we are in general considering an *ensemble* of chains in the partition function equation (10), at the critical condition the thermodynamic properties of the model are dominated by the contribution of the infinite chain. The tension between the walls also diverges at the critical condition, so that it is convenient to define an adimensional tension per monomer, whose value at criticality is given by

$$f = \frac{Fa\beta}{\langle N \rangle} = \frac{-\left(\frac{\partial G}{\partial m}\right)_{z,\omega}}{z \left(\frac{\partial G}{\partial z}\right)_{m,\omega}} = \frac{1}{z_c} \left(\frac{\partial z_c}{\partial m} \right)_\omega. \quad (15)$$

It is apparent in these expression that the tension per monomer at the critical condition is a function of the transfer matrix A only, being independent of the particular initial or final condition, as expected.

2 Numerical results and conclusion

The numerical calculations were done determining, for given values of ω and m , the critical activity z_c . Then we estimated the tension between the walls through equation (15), making the discrete approximation

$$f(m+1/2, \omega) \approx \frac{2}{z_c(m+1, \omega) + z_c(m, \omega)} \times [z_c(m+1, \omega) - z_c(m, \omega)]. \quad (16)$$

As stated above, the dimension of the transfer matrix increases quite rapidly with growing values of m , and this sets a limit for the cases we could consider, which are

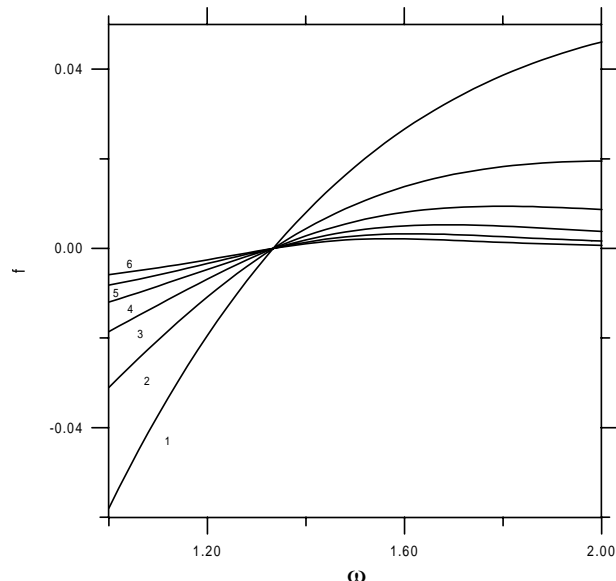


Fig. 2. Ideal chains: Tension f as a function of w for various values of the width m of the strip: (1) $m = 2.5$, (2) $m = 3.5$, (3) $m = 4.5$, (4) $m = 5.5$, (5) $m = 6.5$, (6) $m = 7.5$.

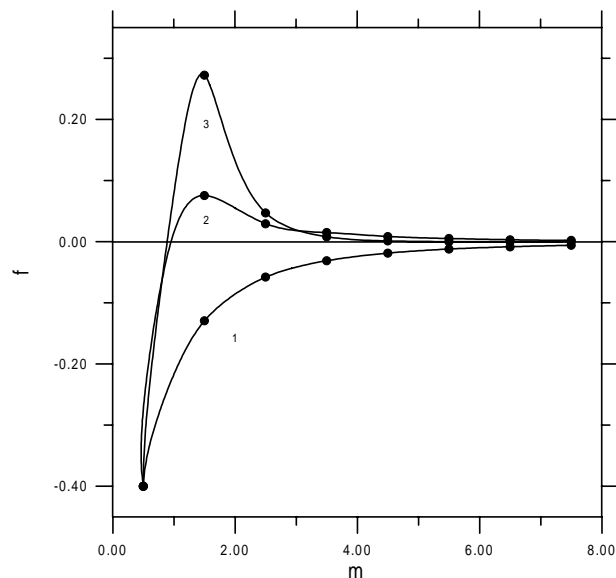


Fig. 3. Ideal chains: Tension f as a function of the distance m between walls, for some values of ω : (1) $\omega = 1$, (2) $\omega = 1.64$, (3) $\omega = 4$. The calculated values, for semi-integer values of m , are indicated, and the lines joining them are just a guide to the eye.

restricted to $m = 0, 1, \dots, 8$. We took advantage of the reflection symmetry in the numerical calculations, but even so the sizes of the matrices for the first ten values of m are 1, 1, 3, 6, 16, 38, 100, 256, 681, and 1805. We also show, for comparison, results for the case of ideal chains, calculated through a procedure similar to the one described above, but with transfer matrices which are linearly growing with m and very sparse [4].

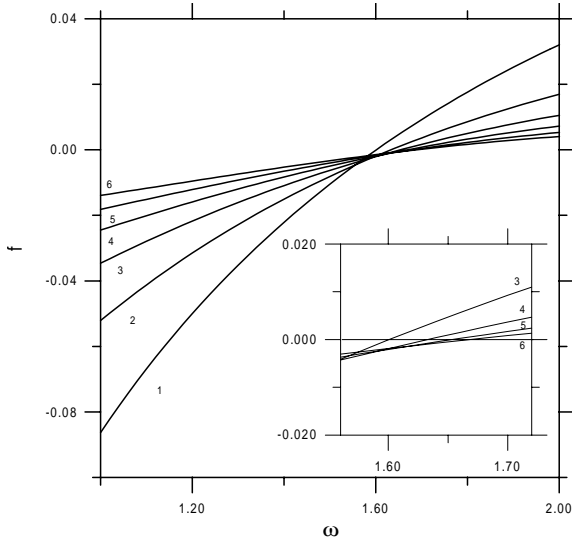


Fig. 4. Self-avoiding chains: Tension f as a function of w for various values of the width m of the strip: (1) $m = 2.5$, (2) $m = 3.5$, (3) $m = 4.5$, (4) $m = 5.5$, (5) $m = 6.5$, (6) $m = 7.5$. In the inset, the region close to $f = 0$ is enlarged.

In Figure 2 we show the tension as a function of ω for ideal chains and $m = 2.5, 3.5, \dots, 7.5$. The results for $m = 0.5$ and $m = 1.5$ were omitted in the graph since they in general assume much larger absolute values and it would be inconvenient to show them in the same scale of the others. For $m = 0.5$ we get the ω independent result $f = -0.4$. As noticed before [4], at $\omega = 4/3$, the tension vanishes for all values of m larger than 0.5. It is remarkable that at this value of ω the adsorption transition for ideal chains on the semi-infinite square lattice happens [12]. Therefore, the tension between the plates is repulsive if $\omega < 4/3$ and attractive if $\omega > 4/3$, for all values of $m > 0.5$. The tension as a function of m for some fixed values of ω is shown in Figure 3.

As said above, for $\omega < 4/3$ the tension is always repulsive, while for $\omega > 4/3$ it is repulsive only at the lowest value $m = 0.5$. Thus, as noted before [4], for $\omega < 4/3$ the equilibrium distance between the walls is infinite, while for $\omega > 4/3$ it is very small.

The results for self-avoiding chains are depicted in Figures 4 and 5. As may be seen in the inset in Figure 4, the curves for tension f as functions of ω as the wall separation m becomes larger. These values of ω were calculated for $m = 2.5, 3.5, \dots, 7.5$ and they are all well below the estimated value for the adsorption transition of self-avoiding chains on the semi-infinite square lattice, which is $\omega_c = 2.041 \pm 0.002$ [13]. As in the case of ideal chains, the curves for $m = 0.5$ and $m = 1.5$ are not shown, due to scale problems. For $m = 0.5$ again we have an ω -independent value $f = -2(3 - \sqrt{5})/(1 + \sqrt{5}) \approx -0.4721$. The tension remains repulsive for all values of m we considered up to $\omega = 1.549375\dots$, where it becomes attractive for $m = 1.5$. We found also, similar to what happens for the case of ideal chains [4], that f is not a monotonically increasing

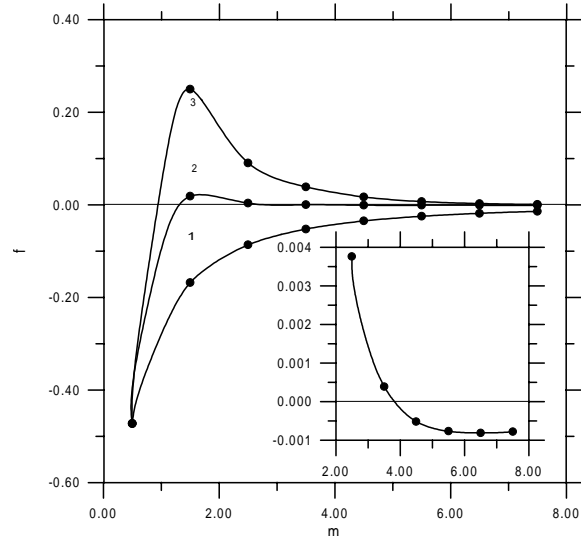


Fig. 5. Self-avoiding chains: Tension f as a function of the distance m between walls, for some values of ω : (1) $\omega = 1$, (2) $\omega = 1.64$, (3) $\omega = 4$. The calculated values, for semi-integer values of m , are indicated, and the lines joining them are just a guide to the eye. In the inset, the region close to the unstable equilibrium point for $\omega = 1.64$ is enlarged.

function of ω , as might be supposed. Actually, the curves $f \times \omega$ pass through a maximum at values of ω larger than the ones shown in Figure 4. As m becomes larger, the maximum occurs for smaller values of ω . It is probable that the explanation of this effect for self-avoiding chains is similar to the one found for ideal chains [4]: As ω becomes larger, the bridges (segments of chains connecting the walls) have less monomers in them, being more stretched, an effect that increases the attractive tension; on the other hand, the number of bridges decreases with growing ω , reducing the attractive tension. The second effect prevails at large values of ω . In the limiting situation $\omega \rightarrow \infty$ the chains are totally adsorbed on the walls and no bridges are present, thus we have $f = 0$.

Finally, in Figure 5 the tension is plotted as a function of m for some values of ω . For $\omega > 1.549375\dots$ one notices that, besides a stable equilibrium point at low values of m , an unstable equilibrium point appears at larger values of m , so as the wall separation gets larger, the tension becomes repulsive again. The unstable equilibrium point is located at higher values of m as ω becomes larger, thus the range of values of m for which the tension is attractive grows with increasing ω . This result is qualitatively different from the one found for ideal chains, where for $\omega > 4/3$ only one equilibrium point was found, the tension being attractive for all $m > 0.5$. A remark connected to this point is that for $\omega = 1$ it was shown [14] that $z_c(m) > z_c(m \rightarrow \infty)$, and we notice that z_c is a monotonically decreasing function of m for $m > 2$ in this case, thus according to equation (15) the tension is repulsive. The bound for $z_c(m)$ is not valid anymore for large enough values of ω .

Since the tension is related to the finite-size behavior of the critical activity, we may ask what can be learned from our results with respect to finite size scaling. The scaling form of the critical activity of self-avoiding chains is expected to be, using the notation of reference [15],

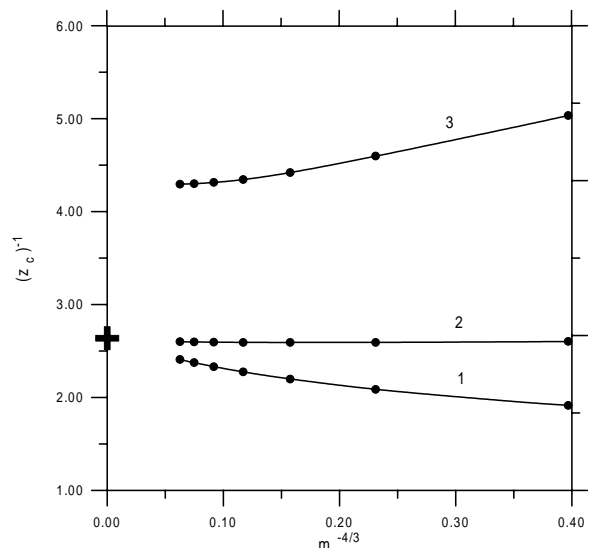
$$z_c(m) \approx \frac{z_c(\infty)}{1 - F_0 a^{-1} m^{-1/\nu}}, \quad (17)$$

where F_0 is universal but a is not. The exponent ν in two dimensions is believed to be equal to $3/4$ [16], while a series estimate of the critical activity for the square lattice is given by $z_c(\infty) = 0.379053 \pm 0.000002$ [17]. The scaling form for the adimensional tension per monomer defined in equation (15) will then be given by

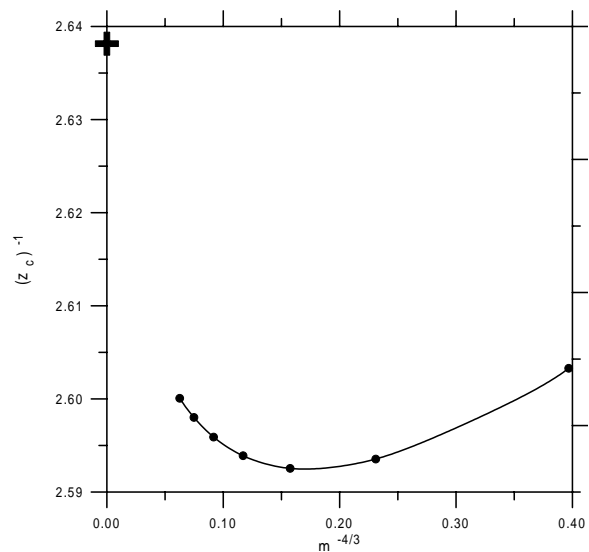
$$f \approx \frac{-F_0 a^{-1} m^{-(1/\nu+1)}}{\nu(1 - F_0 a^{-1} m^{-1/\nu})}. \quad (18)$$

We see that in the scaling regime the force should approach zero monotonically, but the non-universal constant a may be a function of ω . Therefore, it is possible to get into the scaling regime only at widths larger than the one of the unstable equilibrium point. Thus the more interesting properties of the tension between plates, which are the points we center our attention here, happen at widths smaller than the ones where finite size scaling is observed. This may be seen in Figure 6, where the inverse of the critical activities are plotted as functions of $m^{-1/\nu}$, so that a linear region should be found in the scaling regime. While for $\omega = 1$ the data for larger values of m seem to be consistent with the scaling regime, for $\omega = 1.64$ the curve shows a minimum at the unstable equilibrium point, as may be appreciated at a finer scale. For $\omega = 4$ we notice that, although the scaling regime clearly has not been reached yet, the curve is pointing toward another critical activity as $m \rightarrow \infty$. This may be understood as a consequence of the fact that this value of ω is larger than the adsorption value ω_c and the polymerization transition will occur at the neighborhood of the walls at infinite plate separation, so that the proper value of ν to be used in equation (17) would be the one-dimensional value 1 and another critical activity would be reached. The full discussion of the scaling properties of the model are beyond the scope of these work, but we are presently studying them.

In conclusion, we may try to compare our results with previous ones in the literature. Woodward [18] has done a density-functional calculation for an off-lattice athermal model with hard-sphere polymers and an hard-sphere solvent. One must be careful in comparing these kind of results with ours since he considered monodisperse polymers with just 8 monomers, while our results are for a polydisperse set of chains with infinite mean molecular weight. Also, we have not taken the properties of the solvent into account explicitly, and its contribution to the tension between walls. The model treated by Woodward has more parameters to be adjusted than ours, but being athermal it is restricted to



(a)



(b)

Fig. 6. Inverse of the critical activity $(z_c)^{-1}$ as a function of $m^{-4/3}$. The cross indicates the estimate of the two-dimensional value, at $m \rightarrow \infty$. Full circles indicate the calculated values for $m = 2, 3, \dots, 8$ and the lines are guides to the eye. Self-avoiding chains. (a) (1) $\omega = 1$, (2) $\omega = 1.64$, (3) $\omega = 4$. (b) Results for $\omega = 1.64$ in a finer scale.

$w = 1$. We notice that in his model the polymer contribution to the tension shows a behavior which resembles the one for ideal chains at low densities of monomers, but as the densities are increased, oscillations in the tension are obtained, with more than one extremum point. This agrees qualitatively with our results for self-avoiding chains. It should be stressed that our results

are not for a constant density of monomers (fraction of sites of the lattice occupied by monomers). At the critical condition, these fraction is equal to one for $m = 0$, monotonically decreasing to zero in the limit $m \rightarrow \infty$ [11].

Experiments where the force between plates with a polymer melt between them lead to results of a repulsive tension at low plate separation, followed by a very weak attractive tail, which tends to increase as the polymers adsorption on the surfaces becomes larger [19]. The results agree rather well with mean-field theory predictions, which correspond to ideal chains. Tensions which are oscillating as functions of the plate separation are also reported, but only for monodisperse polymer melts with rather low molecular weight [20]. We should remark that since the model for self avoiding chains was solved on a strip defined on a two-dimensional lattice, the effects of the excluded volume interaction should be bigger than the ones observed in a three-dimensional situation.

The model considered here may be changed to include some other effects. The solvent may be introduced explicitly [11], but this leads to larger transfer matrices. Also, semi-flexible chains could be treated. We are presently studying these cases.

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