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LETTER TO THE EDITOR

Self-avoiding walks in a slab with attractive walls

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Abstract

We consider a self-avoiding walk confined between two parallel planes (or lines), with an energy term associated with each vertex of the walk in the confining planes. We allow the energy terms to be different for the top and bottom planes. We use exact enumeration and Monte Carlo methods to investigate the force between the confining planes and how it depends on the width of the slab and on the interaction energy terms. The phase diagram is qualitatively similar to that found for a directed walk model.

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(Some figures in this article are in colour only in the electronic version)

When a polymer molecule in dilute solution is confined between two parallel plates the polymer loses entropy and this results in a repulsive force on the confining plates. This is the essential mechanism of steric stabilization [1] of colloidal dispersions by adsorbed polymer chains on the surfaces of the colloidal particles. As the colloidal particles approach one another the adsorbed polymer molecules exert a repulsive force on the particles due to this loss in configurational entropy. If the polymer is attracted to the two confining plates then the force can be attractive under some conditions. This is the basic mechanism of sensitized flocculation of colloids by adsorbed polymer chains.

These phenomena are also of interest in terms of understanding how a polymer responds to a geometrical constraint, and can be investigated by modelling the polymer in a variety of ways. The simplest possible models are random and directed walk models [2, 3]. One would hope to be able to investigate self-avoiding walk models but rigorous results are only available for the case when the walls only act as a barrier and there are no additional forces [4, 5]. Numerical results are available for this case [6, 7] and also when there are attractive forces with the walls [8, 9]. Stilck and Machado have studied the attractive walls case in two dimensions using transfer matrix techniques [10].

The directed walk model has been studied in detail [3] for the case of a short range interaction of the vertices of the walk with each wall. The interactions with the two walls can be the same or different and can be repulsive or attractive. The model used was closely related to Dyck paths which are directed walks on the square lattice with steps only in the north-east and south-east directions, confined to begin and end on a line (the line $y = 0$, say) and to lie in or on one side of this line (i.e. to have all coordinates with non-negative y-coordinate). In addition the walks were constrained so that no y-coordinate is greater than a fixed value, w. (This is the special case of *loops*, considered in [3].) Suppose that $l_n(u, v, w)$ is the number of such walks with n edges and with $u + 1$ vertices in $y = 0$ and with v vertices in $y = w$. Define the partition function

$$L_n(a, b, w) = \sum_{u,v} l_n(u, v, w) a^u b^v \tag{1}$$

and the corresponding free energy

$$\mathcal{L}_n(a, b, w) = n^{-1} \log L_n(a, b, w). \tag{2}$$

We are interested in the behaviour of the system as a function of the two Boltzmann factors a and b and the width w. For this model the phase diagram was investigated in the large w regime (where $n \to \infty$ for fixed w and then w is taken to be large) [3]. For $a < 2, b < 2$ the force is long ranged and repulsive. There is a zero force curve given by $a + b = ab$ and the force is short ranged and attractive for $a > 1, b > a/(a - 1)$. For $a > 1, 2 < b < a/(a - 1)$, for $a \leqslant 1, b > 2$, for $b > 1, 2 < a < b/(b - 1)$ and for $b \leqslant 1, a > 2$ the force is short ranged and repulsive.

In this letter we present both Monte Carlo and exact enumeration data which suggest that the phase diagram for the self-avoiding walk model is very similar to that found for the directed walk case [3].

We have considered the case of self-avoiding walks on the simple cubic lattice starting at the origin and confined to lie in the slab $0 \leqslant z \leqslant w$ (but without the restriction that the last vertex is in $y = 0$). These correspond to *tails*, considered in [3]. In the large w-limit the phase diagrams of loops and tails are identical for the directed walk model [3]. If $c_n(u, v, w)$ is the number of such self-avoiding walks with n edges, having $u + 1$ vertices in $z = 0$ and v vertices in $z = w$, then we can define the partition function

$$Z_n(a, b, w) = \sum_{u,v} c_n(u, v, w) a^u b^v \tag{3}$$

and the finite n free energy

$$\kappa_n(a, b, w) = n^{-1} \log Z_n(a, b, w). \tag{4}$$

By exactly enumerating all self-avoiding walks with $n \leqslant 21$ we have computed $Z_n(a, b, w)$ and $\kappa_n(a, b, w)$ exactly for these values of n for various values of a, b and w. We define

$$F_n(a, b, w) = \kappa_n(a, b, w + 1) - \kappa_n(a, b, w) \tag{5}$$

which is the discrete version of the force exerted by the walk on the confining planes. In figure 1 we show the dependence of $F_{21}(a, 1, w)$ on a for various values of w. That is, the interaction with the plane $z = w$ has been turned off (by setting $b = 1$) and the walk only interacts with the plane $z = 0$. The force is repulsive for all values of a, and decreases as a increases. This corresponds to an increase in the density of vertices in and near the plane $z = 0$ as a increases and the walk is then less extended in the z-direction. At fixed a the force increases as w decreases indicating that the free energy depends more strongly on w at small

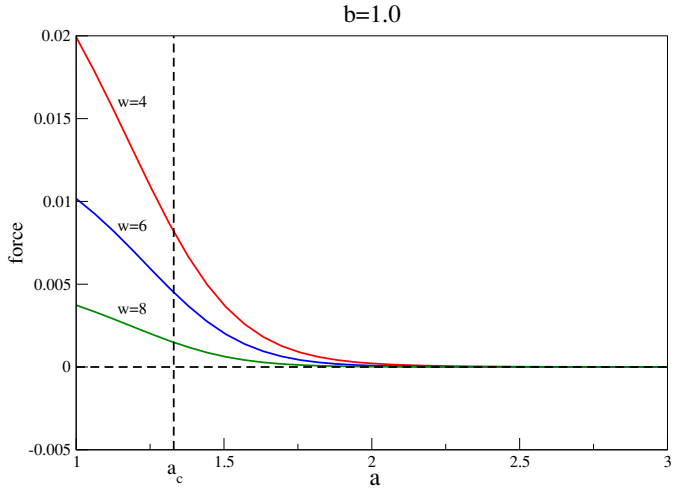

Figure 1. The a-dependence of the force, F, for length $n = 21$ from exact enumeration data for the simple cubic lattice, for $b = 1$ and for three values of w.

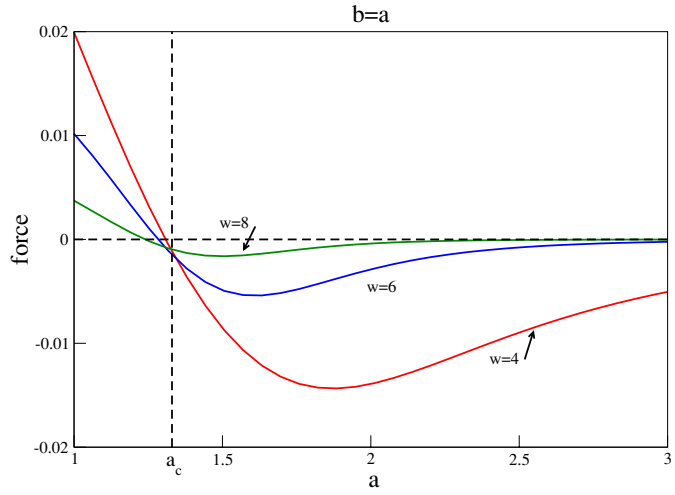

Figure 2. The a-dependence of the force, F, for length $n = 21$ from exact enumeration data for the simple cubic lattice, for $b = a$ and for three values of w.

w than at large w. In figure 2 we set $b = a$ and plot $F_{21}(a, a, w)$ against a for various values of w. The force is repulsive for small values of a, passes through zero, and then becomes attractive for larger values of a. The value of a at which the force is zero is close to the estimated value of the adsorption transition a_c ($a_c \approx \exp[0.288] \approx 1.33$ for the simple cubic lattice) for the single interface problem [11]. The force is (numerically) larger for smaller values of w. For small a the walk is not adsorbed on the confining surfaces and loses entropy when the surfaces are brought together. For larger a the walk is adsorbing on both confining surfaces and the free energy is optimized at smaller separations resulting in an attractive force. This is precisely the behaviour found for the directed walk model [3].

For the case $a = b = 1$ the scaling of the free energy with w was examined by Daoud and de Gennes [12]. They argued that there were two competing length scales, w and n^{ν}, where

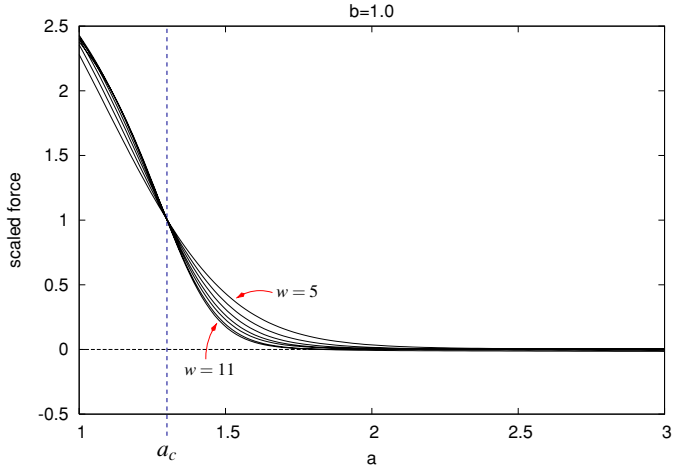

Figure 3. The scaled force, $w^{1+1/\nu}F$, for $n = 128$ for the simple cubic lattice, against a for $b = 1$ and for values of w ranging from 5 to 11.

ν is the exponent characterizing the dimensions (radius of gyration or end-to-end length) of a self-avoiding walk, and that the (extensive) free energy should depend on the ratio of these length scales. That is,

$$\kappa_n(1, 1, w) \sim n^{-1} f(n^{\nu}/w), \tag{6}$$

where they assumed that the function f was a power law, $f(x) = x^{\phi}$. Since $\kappa_n(1, 1, w)$ becomes independent of n in the large n limit this implies that $\phi = 1/\nu$ and hence that $\kappa_n(1, 1, w) \sim w^{-1/\nu}$. The (repulsive) force then scales as

$$F \sim w^{-1-1/\nu}. \tag{7}$$

We also expect this scaling form for all $a, b < a_c$. (This is confirmed by a direct calculation for the directed walk case [3]).

In order to obtain numerical data for larger values of n we have carried out Monte Carlo calculations in which we estimate the free energy as a function of n, a, b and w. For the simple cubic lattice we used the atmosphere method to estimate the free energy [13] and the flatPERM algorithm [14, 15], while for the square lattice we used only the flatPERM algorithm. In three dimensions the results from the two different Monte Carlo algorithms are in excellent agreement with one another. In figure 3 we plot the scaled force, $w^{1+1/\nu}F$, for the simple cubic lattice, against a for $b = 1$, for three values of w. We take ν to be 0.588. For small values of a (i.e. for $a < a_c$) we expect the behaviour predicted by (7) so the results for the different values of w should collapse to a single curve. In fact the collapse is not perfect at these values of w indicating correction to scaling terms for small w which are not included in the above discussion. For larger values of a the force is very small, as expected. In figure 4 we show the scaled force for $b = a$ for various values of w. Again we expect the behaviour of (7) for $a < a_c$ and we see only partial collapse of the data. For larger values of a the force is attractive.

In figure 5 we show the fluctuations in the numbers of visits to the confining planes for the simple cubic lattice, as a function of a and b. The results show strong fluctuations for $a = a_c, b < a_c$, for $b = b_c, a < a_c$ and for $b = a, a > a_c$. We interpret these as remnants of lines of phase transitions in the $w \to \infty$ limit, corresponding to adsorption transitions on the

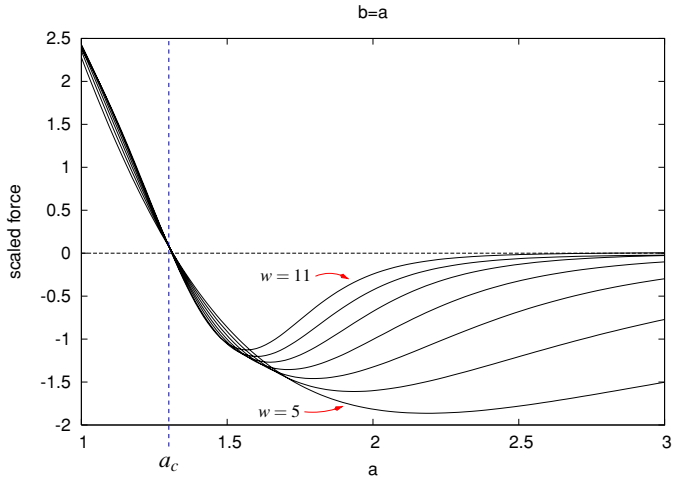

Figure 4. The scaled force, $w^{1+1/\nu} F$, for $n = 128$ for the simple cubic lattice, against a for $b = a$ and for values of w ranging from 5 to 11.

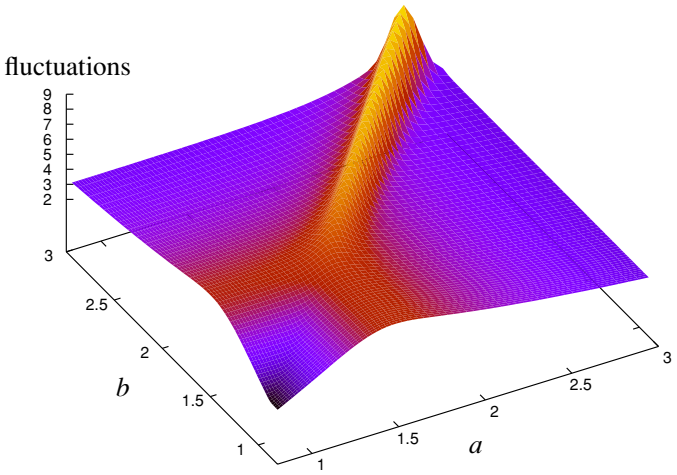

Figure 5. The largest eigenvalue of the matrix of fluctuations in the numbers of visits to the confining planes for the simple cubic lattice as a function of a and b.

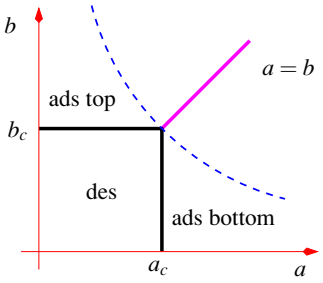

Figure 6. Schematic phase diagram for the problem of polymers in a slab. There are 3 phases: desorbed (des), adsorbed onto the bottom wall (ads bottom) and adsorbed onto the top (ads top). The dashed line is the line of zero force.

two planes, and to a transition from adsorption on one plane to adsorption on the other plane as we cross the line $b = a$. Results for the square lattice show a similar picture.

All of our data are consistent with a phase diagram for the self-avoiding walk problem (see figure 6) which is very similar to that found for the directed walk problem [3]. Further results on the details of the asymptotics will appear elsewhere.

Acknowledgments

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