Chapter 10
Effect of Confinement: Polygons in Strips, Slabs and Rectangles

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10.1 Introduction

In this chapter we will be considering the effect of confining polygons to lie in a bounded geometry. This has already been briefly discussed in Chapters 2 and 3, but here we give many more results. The simplest, non-trivial case is that of SAP on the two-dimensional square lattice $\mathbb{Z}^2$, confined between two parallel lines, say $x = 0$ and $x = w$. This problem is essentially 1-dimensional, and as such is in principle solvable. As we shall show, the solution becomes increasingly unwieldy as the distance w between the parallel lines increases. Stepping up a dimension to the situation in which polygons in the simple-cubic lattice $\mathbb{Z}^3$ are confined between two parallel planes, that is essentially a two-dimensional problem, and as such is not amenable to exact solution.

Self-avoiding walks in slits were first treated theoretically by Daoud and de Gennes [4] in 1977, and numerically by Wall et al. [14] the same year. Wall et al. studied SAW on $\mathbb{Z}^2$, in particular the mean-square end-to-end distance. For a slit of width one they obtained exact results, and also obtained asymptotic results for a slit of width two. Around the same time, Wall and co-workers [13, 15] used Monte Carlo methods to study the width dependence of the growth constant for walks confined to strips of width w. In 1980 Klein [9] calculated the behaviour of SAW and SAP confined to strips in $\mathbb{Z}^2$ of width up to six, based on a transfer matrix formulation.

The interest in the problem arises from two separate aspects. Firstly, there is the intrinsic interest in the effect of geometrical constraints. Secondly, this confined geometry is appropriate to model polymeric properties, such as sensitised flocculation and steric stabilisation, again first discussed in this context by de Gennes [5] in 1979.

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The effect of confinement leads to a loss of configurational entropy, with the consequence that there is a repulsion exerted by the polygon on the confining walls. That this force is repulsive for all values of w was proved by Hammersley and Whittington [7] in 1985, a result that was extended by Janse van Rensburg et al. [8] who showed that the force remains repulsive despite a certain level of interaction with the confining lines. If there is, in addition, an attractive interaction with the walls, there is then a competition between entropic repulsion and the attractive polymer adsorption.

In an earlier paper Di Marzio and Rubin [6] studied a random walk model of a polymer confined between two planes in $\mathbb{Z}^3$. The model included wall–walk interactions. In the absence of these interactions there is the expected loss of configurational entropy, and the walls exert an effective repulsion. If there is an attraction to only one of the two walls, this repulsion was found to persist. If however there is an equal attraction at both walls, then the more interesting situation in which the force is repulsive for weak wall–monomer interactions, but attractive for stronger wall–monomer interactions was found.

In the bulk, it is known (see Chapter 1) that self-avoiding walks and self-avoiding polygons have the same growth constant. However, this is not true for SAW and SAP confined to a slit, as proved by Soteros and Whittington [11]. In fact they proved that the growth constant for polygons in a slit of width w is strictly less than the growth constant for SAW in a slit of the same (finite) width. This is a strictly two-dimensional phenomenon. It is not true in higher dimensions. That is to say SAW and SAP confined to lie between two parallel planes in $\mathbb{Z}^3$ have the same connective constant.

In a thorough and detailed study of SAW in strips, Ahlberg and Janson [1] in 1990 gave a transfer matrix formalism. Denoting the generating function for walks in a strip of width L, as usual, as $C_L(x) = \sum_n c_n^{(L)} x^n$, where $c_n^{(L)}$ is the number of translationally distinct SAW, they proved (a) that $c_n^{(L)} = \alpha\mu_L^n + \mathrm{o}(\mu_L^n)$ as $n \to \infty$, and (b) $c_{n+1}^{(L+1)}/c_n^{(L)} \to \infty$, and (c) $c_n^{(L)}/\mu_L^n$ converges exponentially. They proved similar results for SAP in a slit, including the result of Soteros and Whittington that the growth constant for SAP in a slit of finite width is strictly less than the corresponding result for SAW. They obtained the growth constants for SAW in strips of width up to 10 steps, and, for SAW on a cylinder, in a cylinder up to 10 links in the circular direction. They also gave a detailed study of the properties of the transfer matrix, and obtained a Central Limit Theorem for the endpoint.

Very recently Alvarez et al. [2] studied SAW and SAP in a slit, with wall interactions. For SAP they found that, for any finite value of the wall–monomer interaction term, there is an infinite number of slit widths where a polygon will induce a repulsion between the confining lines.

In Chapter 3 we saw how SAP in a strip are completely encodable by the position of their horizontal edges. Indeed, it was shown that they could be encoded by a finite alphabet, and that alphabet was given for both a strip of width 2 and a strip of width 3. The number of states required to count polygons in a strip of width w grows as 3^w, which prevents this calculation from being pushed to very high values of w. More precisely, Klein [9] has shown that the number of states is given by

$$\frac{w(w+1)}{2}\,{}_2F_3\left(1,\frac{2-w}{2},\frac{1-w}{2};2,3;4\right).$$

This gives a sequence $2,5,12,30,76,196,512,1353,\ldots$ which is growing exponentially, proportional to 3^w. As we saw in Chapter 3 this can be reduced by symmetry. By judicious use of the transfer matrix method, as discussed in Chapter 7, we have extended these encodings to strips of width $w = 17$ for square lattice polygons and for honeycomb lattice polygons (in both lattice directions[1]), and for triangular lattice polygons in strips of width up to 14.

The generating function in each case is rational, and the nature of the singularity at the radius of convergence, which we identify with the critical point, is just a simple pole. For square lattice polygons, we find the degree of the numerator, N and denominator D to be $(N,D) = (0,1), (2,4), (10,14), (34,40)$ for widths $w = 1,2,3,4$ respectively. The value of the smallest real positive zero of the denominator polynomial gives the radius of convergence, and also the reciprocal of the growth constant for polygons, μ_w, and this is a monotone increasing function of w. In this way we obtained the lower bounds $\mu(\text{square}) > 2.4537$, $\mu(\text{honey}) > 1.7759$ and $\mu(\text{tri}) > 3.7272$. (This isn't a particularly efficient way to obtain lower bounds, but is, rather, an additional outcome of the study.)

Daoud and de Gennes [4] developed the scaling theory that predicts how μ_w is expected to scale with width w. Their result was for SAW in a strip, but can be expected to hold mutatis mutandis for polygons in a strip. They find that

$$\log\mu - \log\mu_w \sim const. \times w^{-\phi},$$

where $\phi = 1/\nu = 4/3$. Recall that $\nu = 3/4$ is the mean-square end-to-end distance scaling exponent. For walks confined between planes in $\mathbb{Z}^3$, the same result is expected to hold, except now the value of ν is not known exactly, but to a good approximation is $\nu(3d) \approx 0.57...$ Recall that we have very precise estimates of μ for all lattices (these are more precise in 2d than in 3d). Indeed, for the honeycomb lattice in 2d we believe the exact value to be $\mu(\text{honey}) = \sqrt{2+\sqrt{2}}$.

In Table 10.1 we give the results for the growth constant for strips of width $d = w+1$ sites, (w is the width in bonds), for the square, triangular and honeycomb lattices. The monotone increasing values of μ_d can be readily seen. In Fig. 10.1 we plot $\log\mu - \log\mu_d$ against $\log d$ for the square lattice, and show the solid line of gradient $-4/3$. It can be seen that quite large values of w are required before we reach the asymptotic regime, but that the scaling predictions are well supported by the data. That is to say, the later points do indeed seem to have a locus of the same gradient as the line drawn. The figures for the other lattices are qualitatively similar.

[1] We draw the honeycomb lattice as a brickwork lattice, so the lattice is not symmetrical in the two lattice directions.

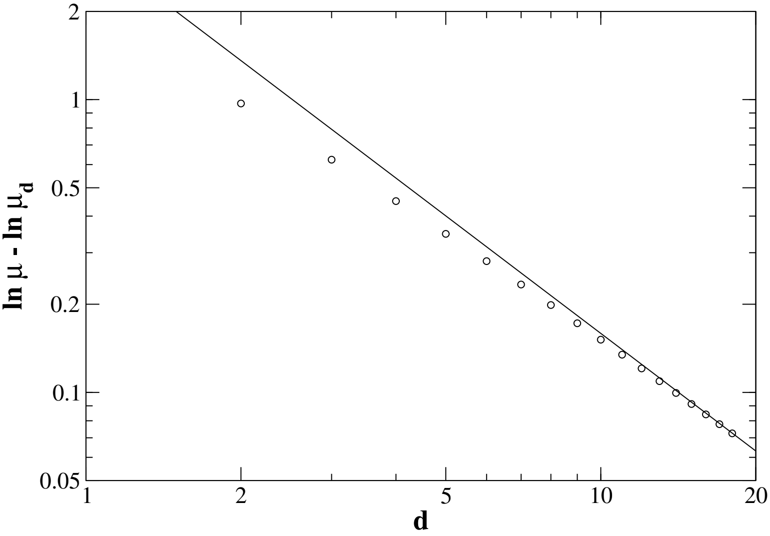

Fig. 10.1 Plot of $\log \mu - \log \mu_d$ vs. d on a logarithmic scale for the square lattice data. The straight line corresponds to the theoretical prediction of gradient $-4/3$.

10.2 Polygons in a Square

Consider now SAW confined to an $L \times L$ square. This problem has a long history, and a detailed discussion can be found in [3]. In that paper it was shown, among

Table 10.1 $d = w + 1$ is the strip width, μ_d is the growth constant for square, triangular and honeycomb (direction 1 and 2) lattice polygons in the strip.

d	μ_d(square)	μ_d(tri)	μ_d(honey1)	μ_d(honey2)
2	1.000000000	1.000000000	1.000000000	1.000000000
3	1.414213562	1.795088688	1.229990405	1.229990405
4	1.681759003	2.328493240	1.374333111	1.411814730
5	1.863069582	2.684771831	1.470190448	1.506504156
6	1.992445913	2.936411124	1.537116598	1.570592201
7	2.088633483	3.121963721	1.585935359	1.616386758
8	2.162502131	3.263502052	1.622845444	1.650489362
9	2.220732353	3.374453146	1.651575171	1.676722086
10	2.267631888	3.463397284	1.674476550	1.697434531
11	2.306090565	3.536045068	1.693096661	1.714142575
12	2.338112184	3.596328876	1.708490122	1.727863827
13	2.365125683	3.647036006	1.721398098	1.739304455
14	2.388174882	3.690191779	1.732355266	1.748968490
15	2.408038380	3.727299874	1.741756176	1.757224477
16	2.425307673		1.749897782	1.764347596
17	2.440439441		1.757007495	1.770547115
18	2.453791386		1.763262171	1.775984775

other things, that the number of SAW starting at $(0,0)$ and ending at (L,L) and never leaving the square, grows as λ^{L^2}. That is to say, if C_L is the number of such walks, then $\lim_{L\to\infty} C_L^{1/L^2} = \lambda$. It was estimated that $\lambda = 1.744550 \pm 0.000005$. A related problem consists of estimating the number of *transverse walks,* defined as SAW that cross the square from any vertex on the left edge of the square (hence the x co-ordinate is 0), to any vertex on the right edge (with x co-ordinate L). In [3] it was proved that if T_L denotes the number of such walks in an $L \times L$ square, then $\lim_{L\to\infty} T_L^{1/L^2} = \lambda$, with the same value of λ as for C_L.

We now consider SAP that span the square. That is to say, one or more edges of the polygon must lie on each edge of the square. As far as we are aware, this problem has not previously been considered. Let P_L denote the number of such polygons. A moment's reflection shows that $P_L < T_L$, and $P_{L+1} > C_L$, as one can readily construct a unique SAP occupying an $(L+1) \times (L+1)$ lattice from a SAW going from $(0,0)$ to (L,L), by the addition of a step from (L,L) to $(L,L+1)$, then another from $(L+1,L+1)$, then a ray from $(L+1,L+1)$, to $(L+1,-1)$, followed by a further ray from $(L+1,-1)$ to $(0-1)$, and then a final step to the origin. In this way we can prove that $\lim_{L\to\infty} P_L^{1/L^2} = \lambda$.

Table 10.2 The number of self-avoiding polygons P_L in a square of size $L \times L$.

L	P_L
1	1
2	5
3	106
4	6074
5	943340
6	419355340
7	554485727288
8	2208574156731474
9	26609978139626497670
10	973224195603423767343946
11	108342096917091380628767818812
12	367632110165285493100682241223688860
13	380442870437494362845946443088614996054 92
14	12008099388785685599269325382154267877752827 2944
15	1155964922833172664443974642986506946314409762614495586
16	339348804164628998142857810063972002009982949540623888989656 82

Several refinements or extensions of this problem remain to be considered. The number of steps (the perimeter) of a SAP in a square varies from a minimum of $4L$ to a maximum of $(L+1)^2$. It would be interesting to study the distribution of perimeters with L. A second aspect amenable to study would be to include an interaction between adjacent monomers of the polygon, and/or with the edges of the square. From the discussion in Chapter 12, and the section below, we have some understanding of what to expect in these cases, but it would still be of interest to see the details.

10.3 Polygons in a Strip Interacting with Walls

In the previous two sections we considered SAP in confined geometries, but apart from confinement, there was no additional constraint imposed by the walls. In this section we consider the situation where there is an interaction associated with edges of the polygon in, or adjacent to, a wall.

Very recently, Alvarez et al [2] have investigated the situation of SAP (and SAW) in strips of width w, interacting with the walls. It is necessary to consider not just the situation *at* the surfaces, but also immediately adjacent to the surfaces if a full range of behaviour is to be observed. This is because polygons are topologically circular. So that if they span a strip, the top edge can never reach the bottom of the strip (this phenomenon is particular to polygons in two dimensions). More precisely, if we define the *top edge* of the polygon as that part of the polygon between the first vertex lying in the top of the slit and the last vertex lying in the top of the slit, then no vertex in the top edge can lie in the bottom of the slit. This topological constraint has been overcome by considering interactions with the second row. This means the top (bottom) can interact with the second layer of the bottom (top). We shall adopt the notation of Alvarez et al. [2], and point out a six-dimensional vector $\mathbf{v} = (v_0, v_{0,1}, v_1, v_{w-1}, v_{w-1,w}, v_w)$ is required in order to keep track of the number of bonds v_0 lying in the slit edge at $y = 0$, v_1 lying in the row $y = 1$ (which is the row immediately above the bottom of the slit), v_w lying in the slit edge at $y = w$, v_{w-1} lying in the row $y = w-1$ (which is the row immediately below the top of the slit). Finally $v_{0,1}$ is the number of *vertical* bonds between $y = 0$ and $y = 1$, and $v_{w-1,w}$ is the number of *vertical* bonds between $y = w-1$ and $y = w$. We also introduce two corresponding vectors of Boltzmann factors, $\mathbf{a} = (a_0, a_{0,1}, a_1)$ and $\mathbf{b} = (b_{t-1}, b_{t-1,t}, b_t)$. Then if $p_n(\mathbf{v}, w)$ is the number of SAP in a slit of width w with n edges and restricted by having edges in various places as specified by $\mathbf{v}$, the partition function is

$$Z_n(\mathbf{a},\mathbf{b},w) = \sum_{\mathbf{v}} c_n(\mathbf{v},w) a_0^{v_0} a_{0,1}^{v_{0,1}} a_1^{v_1} b_{t-1}^{v_{w-1}} b_{t-1,t}^{v_{w-1,w}} b_t^{v_w}. \tag{10.1}$$

The grand canonical partition function is then given by

$$H(\mathbf{a},\mathbf{b},w) = \sum_{n=0}^{\infty} Z_n(\mathbf{a},\mathbf{b},w) z^n, \tag{10.2}$$

and the corresponding free energy is

$$\kappa(\mathbf{a},\mathbf{b},w) = \lim_{n\to\infty} n^{-1} \log Z_n(\mathbf{a},\mathbf{b},w), \tag{10.3}$$

while the force exerted by the polygon on the confining walls is

$$f(\mathbf{a},\mathbf{b},w) := \frac{\partial}{\partial w} \kappa(\mathbf{a},\mathbf{b},w). \tag{10.4}$$

Alvarez *et al.* considered four special cases, which were:
(a) $a_{0,1} = a_1 = b_{t-1} = b_{t-1,t} = 1$, corresponding to a *single layer at both walls.* Here we have switched off interactions in the second layer, both at the top and at the bottom, and only interactions in the surfaces take place.
(b) $a_{0,1} = a_1 = b_{t-1,t} = 1$, and $b_{t-1} = b_t = b$ corresponding to a *double layer at the top wall.* Here the interactions occur with the top and next-to-top layer, and also with the bottom layer. All other interactions are switched off.
(c) $a_{0,1} = b_{t-1,t} = 1$, $a_0 = a_1 = a$ and $b_{t-1} = b_t = b$ corresponding to a *double layer at both walls.* Here the interactions occur with the top and next-to-top layer, and also with the bottom and next-to-bottom layer. All other interactions (between the two top and between the two bottom layers) are switched off.
(d) $a_0 = a_{0,1} = a_1 = a$, and $b_{t-1} = b_{t-1,t} = b_t = b$ corresponding to *fully interacting double layers.* Here all interactions are on. The only restriction is that the interactions are all equal at the top, and all equal at the bottom.

Series expansions by use of the transfer matrix method (see Chapter 7) were obtained for strips up to width 9. Two useful lemmas were also proved. They are:

Lemma 1 For SAP in a slit in case (a), we have for any width $w > 0$ that the free energy difference produced by increasing the width by at least w units is non-negative. That is to say

$$\kappa(\mathbf{a},\mathbf{b},w+i) - \kappa(\mathbf{a},\mathbf{b},w) \geq 0$$

for any integer $i > w$.

Lemma 2 There are infinitely many values of w for which the force for SAP in a slit of width w in case (a) is always non-negative.

In Fig. 10.2 we show a plot of the force with $a = b$ line for SAP in slits of various widths in the single layer case (a). It is clear that the forces are always positive, corresponding to a purely repulsive regime. This observation is consistent with the above lemma. The result may indeed be true for all w, but this has not been proved. Also note that the force quickly drops off as a increases.

The case of a double layer at the top wall, case (b) above, overcomes the shielding effect of case (a), in which topology prevents the top of the polygon reaching the bottom wall (and vice versa). SAPs now exhibit both an attractive and a repulsive regime. In Fig. 10.3 we show the zero-force curve for SAP in slits of various widths. The positive force regime (repulsive) is to the S-W of the curves, while the attractive regime is to the N-E. The minimum we observe means we have *re-entrant* behaviour. For wall interaction parameter $b = 3$ say, as we increase the value of a, the force changes from repulsive for small a, then to attractive for intermediate values of a, then back to repulsive for large values of a.

Figure 10.4 shows the force along the $a = b$ line for SAP in slits of various widths in case (b). Again we see that for small values of the wall interaction parameters, the force is repulsive, but as the interaction strength increases, it becomes attractive. This double layer model overcomes the screening that prevents the formation of an attractive regime in the single layer case.

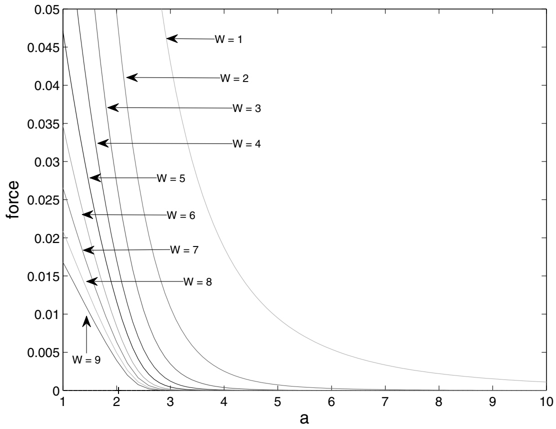

Fig. 10.2 Force along the $a = b$ line for SAP in slits of various widths in the single layer case. Note the absence of any attractive regime (corresponding to a negative force).

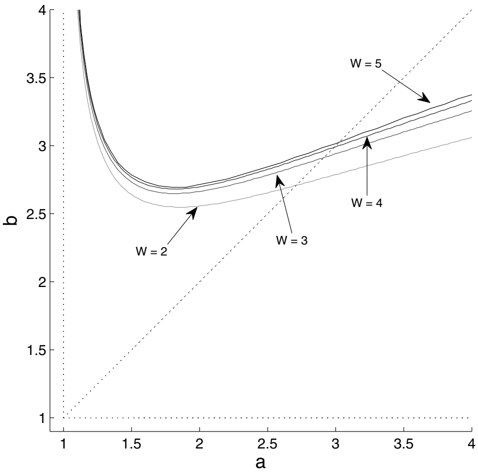

Fig. 10.3 Zero-force curve for SAP in slits of various widths in the case of a double layer at the top wall and a single layer at the bottom wall. The two intersections with the line $b = 3$ signals *re-entrant* behaviour.

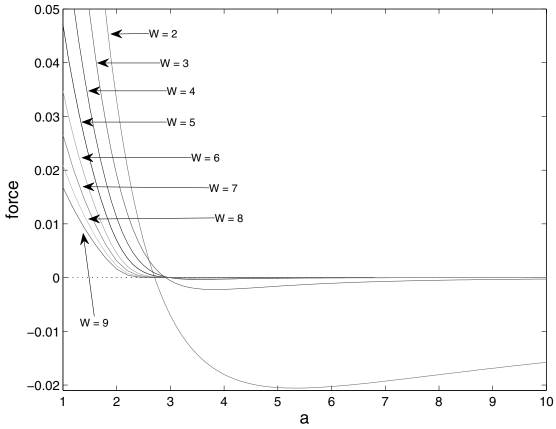

Fig. 10.4 Force along the $a = b$ line for SAP in slits of various widths in the case of a double layer at the top wall and a single layer at the bottom wall. Both attractive and repulsive regimes are evident.

The next situation considered is that of a double layer at both walls. In Fig. 10.5 we show the zero-force curve for SAP in slits of various widths. Unlike the previous case, we observe an expected symmetry about the line $a = b$. As in the previous case, the positive force regime (repulsive) is to the S-W of the curves, while the attractive regime is to the N-E. It is unclear whether the zero-force point along the line $a = b$ diverges as the strip width increases.

The next figure, Fig. 10.6, plots the force along the $a = b$ line for SAP in slits of various widths. Again, both attractive and repulsive regimes are seen. As the width increases, the attractive force is seen to become rather weak.

The final case considered has all interactions switched on, but with the restriction that all the interactions at the top wall are equal, as are all the interactions at the bottom wall. In Fig. 10.7 we plot the zero-force curve for SAP in slits of various widths. The picture looks qualitatively the same as Fig. 10.5, with re-entrant behaviour evident in some regions of the phase diagram.

In Fig. 10.8 the force along the $a = b$ line for SAP of various widths is shown. Again, we see qualitative similarity to the previous double layer case, and the remarks made about that situation apply here too.

In [2] Alvarez *et al.* give a similar analysis for SAW in strips. They observe some significant differences between SAW and SAP. These differences are beyond the scope of this chapter, and are also likely to be confined to the two-dimensional case, so we refer the interested reader to their article.

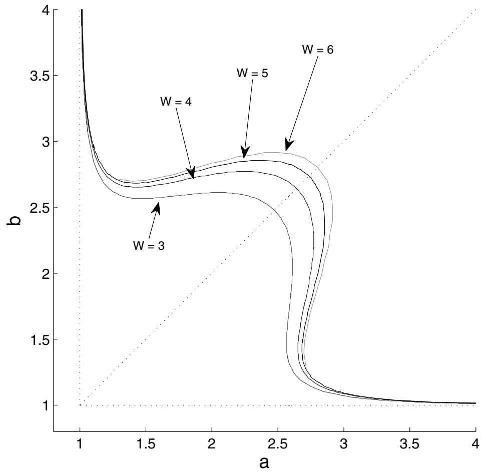

Fig. 10.5 Zero-force curve for SAP in slits of various widths in the case of double layers at both walls. Both *re-entrant* behaviour and symmetry about the line $a = b$ are evident.

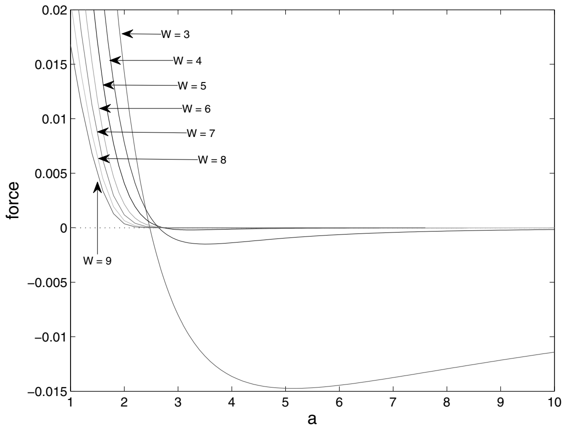

Fig. 10.6 Force along the $a = b$ line for SAP in slits of various widths in the case of double layers at both walls. Both attractive and repulsive regimes are evident.

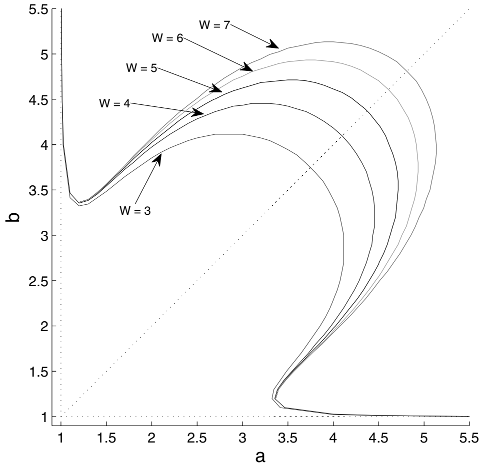

Fig. 10.7 Zero-force curve for SAP in slits of various widths in the case of fully interacting double layers at both walls. Both *re-entrant* behaviour and symmetry about the line $a = b$ are evident.

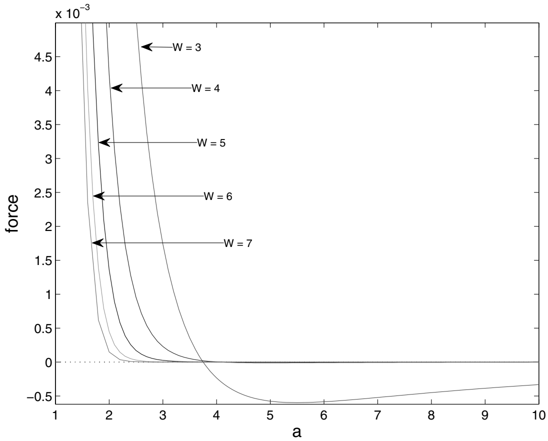

Fig. 10.8 Force along the $a = b$ line for SAP in slits of various widths in the case of fully interacting double layers at both walls. Both attractive and repulsive regimes are evident, though the attractive regime declines with increasing width.

10.4 Conclusion

The consequences of confining SAP (and SAW) to strips/slabs/prisms clearly produces a rich set of both combinatorial results and models of physical, and indeed biological interest. The fact that regimes can change from attractive to repulsive, and back, opens up the possibility of constructing simple models with quite complex behaviour. More significantly perhaps, it means that it is not necessary to postulate complex models to explain complex behaviour. The extension of the study of Alvarez *et al.* [2], discussed above, to three dimensions, would be extremely interesting, but is probably beyond current computational resources.

References

1. Alm S E and Janson S, (1990) Random self-avoiding walks on one dimensional lattices Commun. Statist-Stochastic Models, **6** (2), 189-212
2. Alvarez J, Janse van Rensburg E J, Soteros E G and Whittington, S G (2008) Self avoiding polygons and walks in slits J. Phys A: Math. Gen, **41**
3. Bousquet-Mélou, M, Guttmann, A J and Jensen, I, (2005) Self-avoiding walks crossing a square J. Phys A: Math. Gen, **38** 9159-9181.
4. Daoud, M and de Gennes P G (1977) Statistics of macromolecular solutions trapped in small pores J. de Physique **38** 85-93
5. deGennes P G (1979) Scaling concepts in Polymer Physics (Ithaca: Cornell University Press)
6. Di Marzio E A and Rubin R J (1971) Adsorption of a chain polymer between two plates J. Chem. Phys, **55** 4318-36.
7. Hammersley J M and Whittington S G (1985) Self-avoiding walks in wedges J. Phys A: Math. Gen, **18** 101-11
8. Janse van Rensburg E J, Orlandini E and Whittington, S G (2006) Self-avoiding walks in a slab: rigorous results J. Phys A: Math. Gen, **39** 13869-13902.
9. Klein, D (1980) Asymptotic distributions for self-avoiding walks constrained to strips, cylinders and tubes J. Stat. Phys **23** 561-86.
10. Martin, R, Orlandini E, Owczarek A L, Rechnitzer A and Whittington, S G Exact enumerations and Monte Carlo results for self avoiding walks in a slab, (2007) J. Phys A: Math. Gen, **40** 7509-21.
11. Soteros C E and Whittington S G (1988) Polygons and stars in a slit geometry J. Phys A: Math. Gen, **21** L857-861.
12. Stilck J F and Machado K D Tension of polymers in a strip (1998) Eur. Phys. J. B **5** 899-904.
13. Wall, F T, Mandel, F and Chin J C (1976) Self-avoiding random walks subject to external spatial constraints J. Chem. Phys, **65** 2231-2234.
14. Wall, F T, Seitz W A and Chin J C (1977) Self-avoiding walks subject to boundary constraints J. Chem. Phys, **67** 434-8.
15. Wall, F T, Seitz W A Chin J C and deGennes P G (1978) Statistics of self-avoiding walks confined to strips and capillaries Proc. Nat. Acad. Sci **75** no 5 2069-70.