

## Modelling the adsorption of a polymer subject to an elongational force by directed walk models

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**Abstract** We discuss several different directed walk models of a homopolymer adsorbing at a surface when the polymer is subject to an elongational force which hinders the adsorption. These models have the advantage that, within the generating function approach, they can often be solved exactly and that in the stretching regime they give a fair representation of the configurational properties of the polymer. By using combinatorial arguments we analyse how the critical temperature for adsorption depends on the magnitude of the applied force and show that the order of the adsorption transition changes from continuous to first order when a force is applied. We discuss which are the minimal ingredients to add into the model in order to obtain a reentrant phase diagram similar to the one observed in models of DNA mechanical denaturation. Another advantage in using directed walk models is that they can be generalized to study, to some extent, the adsorption transition of random copolymers. Indeed, despite the fact that the quenched model cannot be solved exactly we show that a partial knowledge of the full random problem can be obtained by resorting to an approximation in which the quenched average is approximated by a partial annealing procedure, the so-called Morita approximation.

**Keywords** Polymer conformation · Critical point phenomena in polymer physics · Exact methods is studies of phase transitions

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## 1 Introduction

In recent years, the mechanical properties of individual polymers and filaments have thoroughly been investigated experimentally [1,2], thanks to the rapid development of micromanipulation techniques such as optical tweezers [3,4] and atomic force microscopy (AFM) [5,6]. Experiments such as the stretching of single DNA polymers or the force-induced desorption from an attractive surface enhance the possibility of understanding the physical properties of the single molecule. Moreover the underlying physical systems are simple enough to be fairly described by theoretical models that, to some extent, can be solved analytically or explored numerically. This is the case, for example, of the mechanical denaturation of duplex DNA [7] for which the temperature dependence of the critical force  $f_c(T)$  required for unzipping has been studied for a variety of models and the phase diagram has been derived in the  $(f_c, T)$ -plane using exactly solvable models, scaling arguments and numerical approaches [8–11].

A simpler situation which is amenable to theoretical treatment, and which could also be investigated experimentally by micromanipulation techniques, is the mechanical desorption of a polymer from an attracting surface. One can think of a linear polymer molecule attached at one end to an impenetrable surface at which the polymer can adsorb (i.e., there is an attractive interaction between the monomers and the surface). In addition, a force is applied to the other end of the polymer in a direction perpendicular to the surface. This applied force favours desorption and one expects a critical force,  $f_c(T)$ , for desorption which depends on the temperature  $T$ . At fixed  $T$ , if the force is less than  $f_c(T)$  the polymer will be adsorbed, while if the force is larger than  $f_c(T)$  the polymer will be desorbed. Hence the critical force curve  $f_c(T)$  can be regarded as a phase boundary in the  $(T, f)$ -plane.

The mechanical desorption of a polymer from an attractive surface can be seen as a generalization of polymer adsorption, a problem whose statistical mechanics has been studied extensively in the last decades [12] (see also [13,14] for reviews). In this respect the generating function methods applied on directed walk models have proved very useful in investigating analytically the equilibrium phase diagram of the polymer adsorption problem [15–18].

Here we follow this approach by modelling the polymer by a directed walk either in two dimensions with the surface being a line or in three dimensions where the surface is modelled by a plane. First, we consider two different classes of directed walks in two dimensions, related to Dyck paths (Sect. 2) and to Motzkin paths (Sect. 3), and use combinatorial methods to derive the form of the generating function for each model. By looking at the singularity structure of the generating functions [19] we derive the form of the phase diagram and discuss the nature of the adsorption transition both with and without an applied force [20]. We show that the transition changes from being continuous to first order when a force is applied. We then consider a partially directed model in three dimensions and show that this model exhibits a reentrant phase diagram (Sect. 4). A sufficient condition for the re-entrance can be given by a simple argument valid in the low temperature limit (see Sect. 5). In Sect. 6 we show how the above approach can be generalized to the case of adsorption of random copolymers subject to a force. The final Section is devoted to conclusions and discussions.

## 2 Adsorption at an impenetrable surface: a Dyck path model

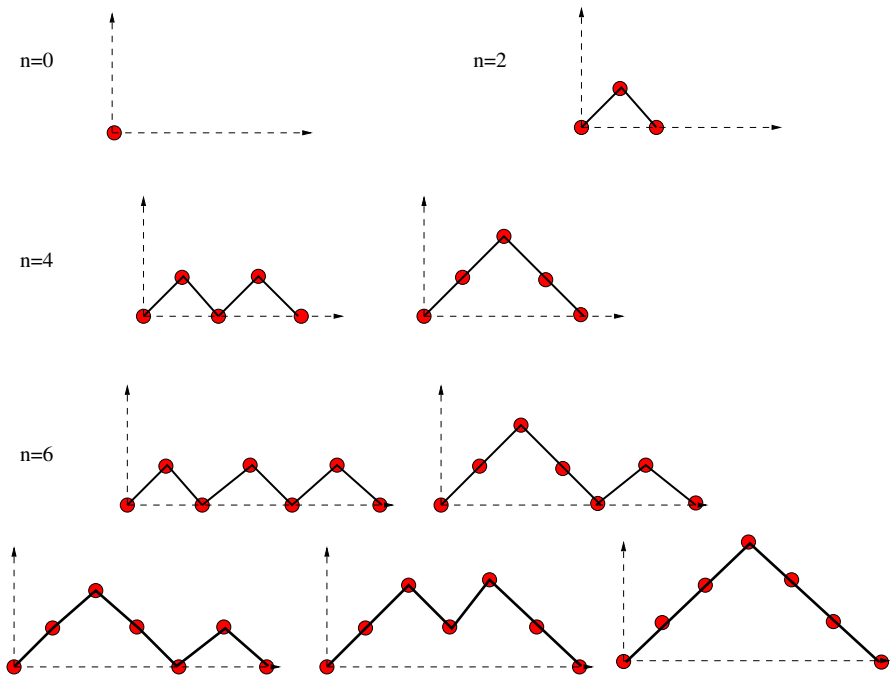
The simplest model of the conformation of a polymer interacting with an impenetrable surface is a Dyck path. Consider the square lattice,  $Z^2$ , i.e. the integer lattice in Euclidean-2-space. We attach a coordinate system  $(x_1, x_2)$  where  $x_1$  and  $x_2$  are integers and we define  $x_2 = 0$  as the line at which adsorption can occur. A Dyck path is a directed walk on  $Z^2$  which obeys the following constraints:

1. The walk starts at the origin and all vertices have non-negative  $x_2$  coordinates.
2. The possible steps are  $(1, \pm 1)$ .
3. The last vertex of the walk has zero  $x_2$  coordinate.

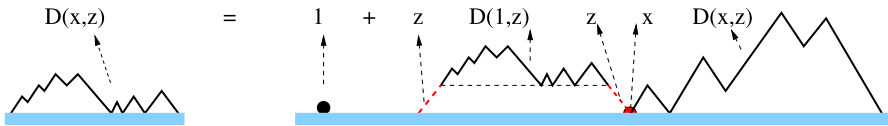
If we write  $d_n$  for the number of distinct Dyck paths with  $n$  edges and adopt the convention that  $d_0 = 1$ , then  $d_2 = 1$ ,  $d_4 = 2$ ,  $d_6 = 5$ , etc. (see Fig. 1). Let us define the generating function of the numbers of Dyck paths as

$$D(z) = \sum_n d_n z^n \quad (1)$$

where  $z$  is conjugate to the number of edges,  $n$ . Clearly a Dyck path can be made by a single vertex. On the other hand a generic Dyck path with  $n > 0$  is a path that leaves the line  $x_2 = 0$ , behaves as a translated (at  $x_2 = 1$ ) Dyck path, return to  $x_2 = 0$  and can be completed by adding another Dyck path. This factorization argument gives the recurrence relation



**Fig. 1** Examples of Dyck paths for the smallest values of  $n$



**Fig. 2** The factorization property of the generating function  $D(x, z)$

$$D(z) = 1 + z^2 D(z)^2. \tag{2}$$

This gives

$$D(z) = \frac{1 + \sqrt{1 - 4z^2}}{2z^2} \tag{3}$$

showing that  $D(z)$  has a singularity on the positive real axis at  $z = 1/2$  which corresponds to the fact that  $\lim_{n \rightarrow \infty} d_n^{1/n} = 2$ . In other words there are about  $2^n$  Dick paths with  $n$  edges, for sufficiently large  $n$ . Dyck paths can be easily modified to produce a simple model of polymer adsorption at an impenetrable surface. This can be done by partitioning Dyck paths according to their number of vertices having  $x_2 = 0$ . Let  $d_n(v)$  be the number of Dick paths with  $n$  edges having  $v + 1$  vertices in the line  $x_2 = 0$ . We say that the walk *visits* the adsorbing line  $v$  times (one vertex is the origin and does not count), or that it has  $v$  visits. By using the factorization argument of Fig. 2, the corresponding generating function

$$D(x, z) = \sum_{v,n} d_n(v) x^v z^n \tag{4}$$

it is shown to satisfy the equation [20]

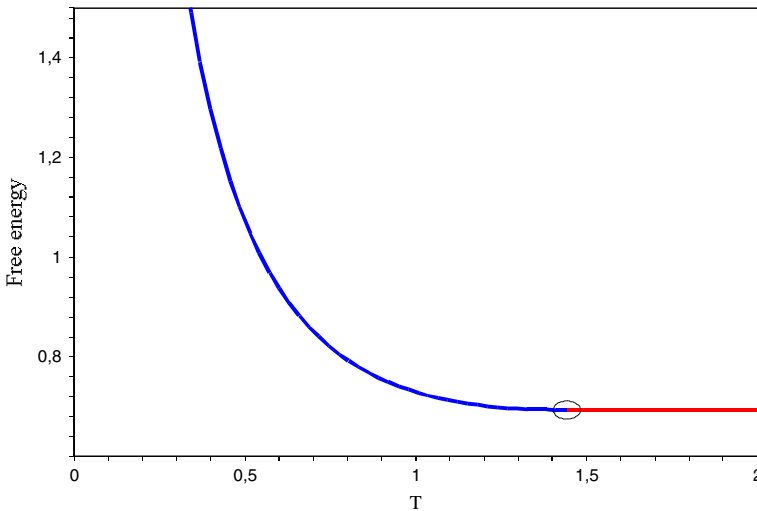
$$D(x, z) = 1 + xz^2 D(1, z) D(x, z). \tag{5}$$

Since  $D(1, z) = D(z)$  Eq. 5 gives

$$D(x, z) = \frac{2}{2 - x(1 - \sqrt{1 - 4z^2})}. \tag{6}$$

The generating function (6) has a square root singularity at  $z_1 = 1/2$  and a pole at  $z = z_2(x)$  corresponding to a zero of the denominator. These two singularities meet at  $x = x_c$ . For  $x < x_c$  the dominant singularity  $z_d$  is  $z_1$  and the walk is in the *desorbed phase*. For  $x > x_c$   $z_d = z_2(x)$  and the walk is in the *adsorbed phase*. The value  $x = x_c$  for which  $z_1 = z_2(x_c)$  gives the adsorption transition point for Dyck paths. To introduce the temperature parameter explicitly into the description the substitution

$$x = e^{-\epsilon/k_B T} \tag{7}$$



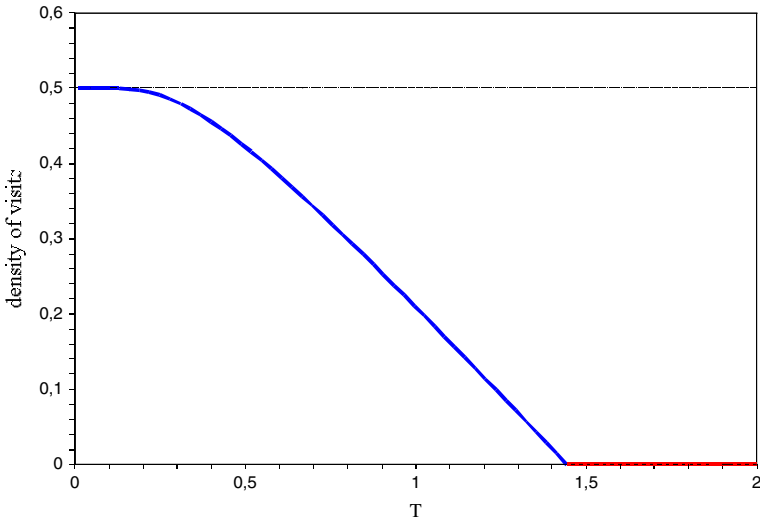
**Fig. 3** Temperature dependence of the free energy for adsorbing walks related to Dyck paths. The circle encloses the location of the adsorption point at  $T = T_c = 1/\log 2$

is considered. Without loss of generality we will work in units where  $k_B = 1$  and set  $\epsilon = -1$  so that  $x = e^{1/T}$ . Figure 3 shows the limiting free energy  $F(T) = -\log z_d(T)$  as a function of  $T$  for the adsorption problem in the Dyck path description. As expected,  $F(T)$  is a convex function of  $T$  that is constant for  $T > T_c = 1/\log(x_c) = 1/\log 2$  and increases as  $T$  decreases for  $T < T_c$ . The density of visits,  $\rho(T)$ , is then simply given by the first derivative of  $F(T)$  and its behaviour is shown in Fig. 4. As expected, for  $T > T_c$  (desorbed phase) the fraction of visits is zero whereas for  $T < T_c$  (adsorbed phase)  $\rho(T)$  increases as  $T$  decreases reaching its limiting value  $1/2$  as  $T \rightarrow 0$ . Note that the value  $1/2$  reflects the fact that for Dyck paths only half of the vertices may, at most, lie on the  $x_2 = 0$  line. From Fig. 4 it is also clear that the adsorption transition is at least a second order phase transition. Finally one can also calculate the value of the crossover exponent  $\phi$  describing the behaviour of  $F(T)$  as  $T \rightarrow T_c^-$  [19]

$$F(T) - F(T_c) \sim (T - T_c)^{1/\phi}. \quad (8)$$

A straightforward calculation shows that for adsorbing Dyck paths  $\phi = 1/2$ .

In order to take into account the effect of an elongational force applied at one extremity of the polymer the above model must be slightly modified as follows. The constraint of the walk ending at  $x_2 = 0$  is relaxed and the Dyck path model is generalized to the one in which paths can have their final vertex at an arbitrary  $x_2 = h$  (see Fig. 5 for an example). Clearly the pure Dyck path model corresponds to the special case  $h = 0$ . Suppose that the number of such  $n$ -edge walks with  $v + 1$  vertices in  $x_2 = 0$ , having their last vertex with  $x_2$ -coordinate equal to  $h$ , is  $b_n(v, h)$ . Define the generating function



**Fig. 4** Temperature dependence of the density of visits for adsorbing walks related to Dyck paths

$$B(x, y, z) = \sum_{v,h,n} b_n(v, h)x^v y^h z^n. \tag{9}$$

Using a factorization argument similar to the one shown in Fig. 2 we get

$$B(x, y, z) = D(x, z)[1 + yzB(1, y, z)]. \tag{10}$$

By putting  $x = 1$  Eq. 10 can be solved for  $B(1, y, z)$  and we obtain the final result [20]

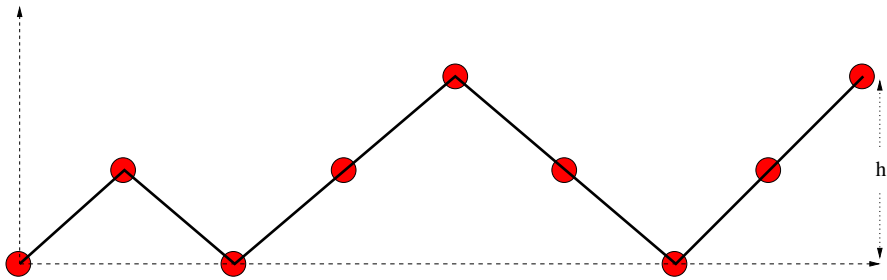
$$B(x, y, z) = \frac{4z}{(2 - x + x\sqrt{1 - 4z^2})(2z - y + y\sqrt{1 - 4z^2})}. \tag{11}$$

This generating function has a square root singularity when  $z = 1/2$  and two other singularities when  $2 - x + x\sqrt{1 - 4z^2} = 0$  and when  $2z - y + y\sqrt{1 - 4z^2} = 0$ . The square root singularity corresponds to the desorbed phase. The adsorption is controlled by whichever of the other two singularities is closest to the origin. We therefore solve each of these two equations for  $z$  to find two critical surfaces

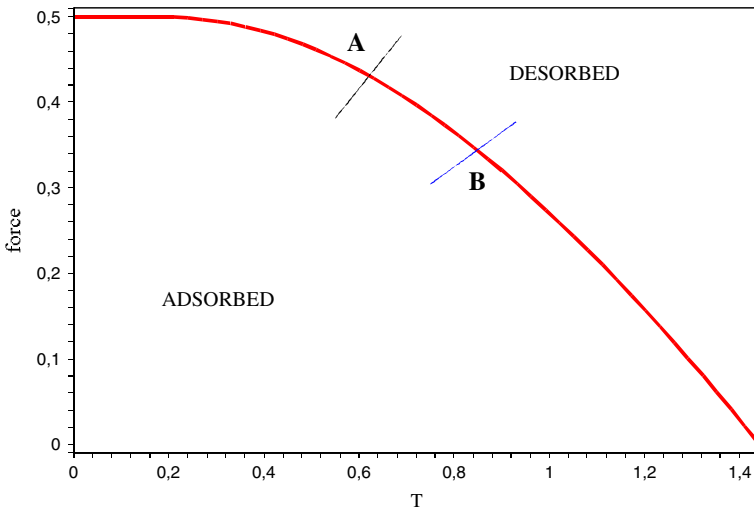
$$z_c^{(1)}(y) = \frac{y}{y^2 + 1} \tag{12}$$

and

$$z_c^{(2)}(x) = \frac{\sqrt{x - 1}}{x}. \tag{13}$$



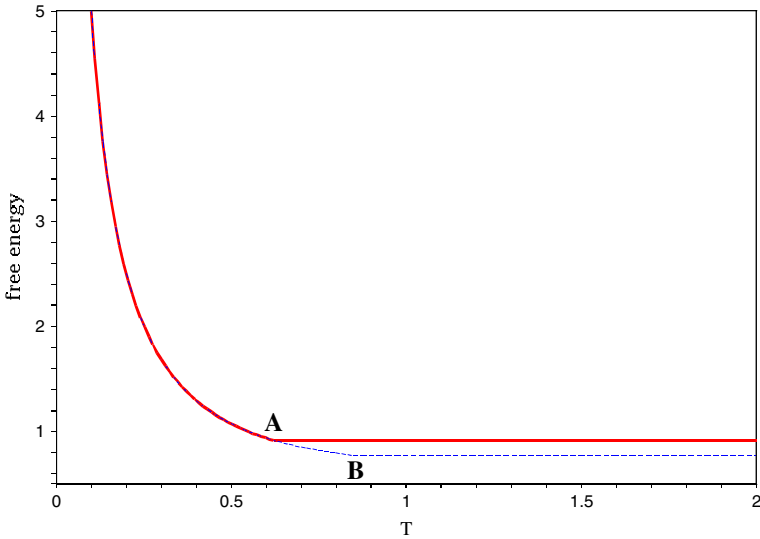
**Fig. 5** Example of a Dyck path with  $n = 8$  edges,  $v = 2$  visits and the last vertex with  $x_2 = 2$



**Fig. 6** Force–temperature phase diagram for adsorbing walks related to Dyck paths. Line A and line B represent, respectively, the directions along which we cross the mechanical desorption curve in the next figures

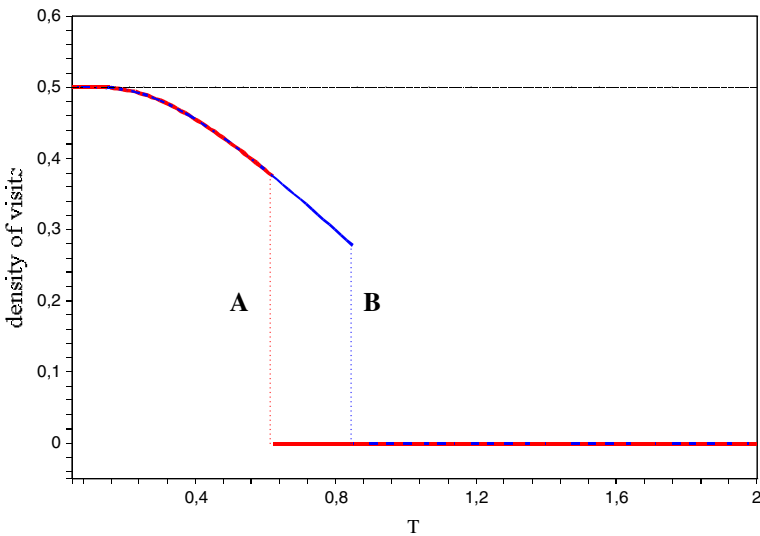
Note that one singularity depends on  $x$  and the other on  $y$ . The phase boundary in the  $(x, y)$ -plane is determined by the condition that  $z_c^{(1)}(y) = z_c^{(2)}(x)$  which gives  $y_c(x) = \sqrt{x - 1}$ . To map the problem into the force–temperature plane we consider  $y = e^{f/T}$  and  $x = e^{1/T}$  where  $T$  is still the temperature and  $f$  is the applied force. This choice of  $y$  is equivalent to setting the value of  $h$  equal to zero when there is no applied force and this is justified because the limiting free energy with no force, at constant  $h$ , is independent of  $h$  for any finite  $h$ . With these substitutions we can plot the phase diagram in the  $(T, f)$ -plane as shown in Fig. 6.

For  $f = 0$  we have the pure adsorption problem (see Eq. 6) with the adsorption point at  $T_c(0) = 1/\log 2$ . Note that the critical force is a monotonically decreasing function of temperature and that, as  $T \rightarrow 0^+$   $f \rightarrow 1/2$  with zero slope. This again reflects the fact that at most half of the vertices can be in the line  $x_2 = 0$  for Dyck paths. It is interesting to explore the equilibrium properties of the model as we cross the critical line  $f_c(T)$ , say for example, at  $f = T \log 2$  and  $f = T \log 1.5$ .



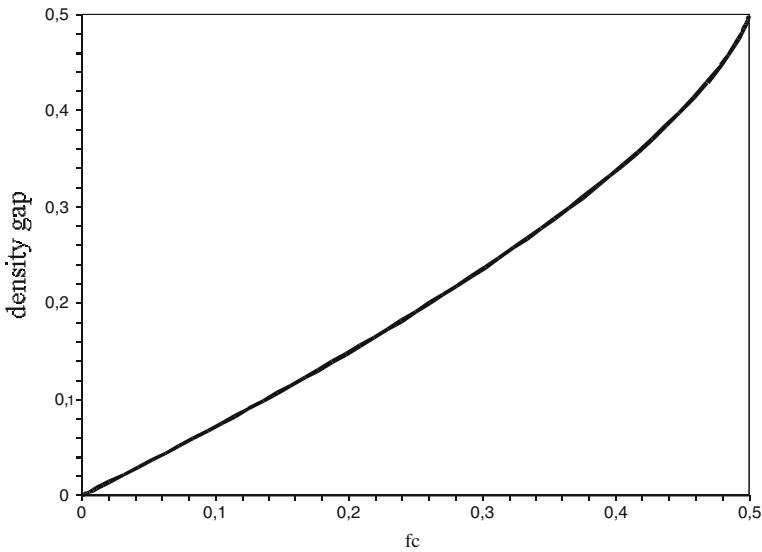
**Fig. 7** Temperature dependence of the free energy as we cross the critical force along the lines  $f = T \log 2$  (A, solid curve) and  $f = T \log 1.5$  (B, dashed line)

Figure 7 shows the limiting free energy as a function of  $T$  for these cases. At first sight the free energy functions for  $f > 0$  look similar to one with no applied force (see Fig. 3), the only difference being the shift of the transition point towards lower values of  $T$ . This is reasonable since the force tends to desorb the polymer. If on the other hand



**Fig. 8** Temperature dependence of the density of visits as we cross the critical force curve along the lines  $f = T \log 2$  (A) and  $f = T \log 1.5$  (B). The density gap at the mechanical desorption transition decreases as  $f$  decreases





**Fig. 9** Density gap at the adsorption transition point as a function of the critical force  $f_c$

one looks at the temperature behaviour of the limiting density of visits an important difference with respect to the  $f = 0$  case is observed since  $\rho(T)$  is not any more a continuous function of  $T$  but presents a finite discontinuity at  $T = T_c(f)$  (see Fig. 8). This discontinuity is present for any value of  $f > 0$  and is a clear evidence that the imposition of an elongation force changes the nature of the adsorption transition from continuous to first order. The size of the discontinuity depends on  $f$  and increases as the critical force increases (see Fig. 9). As expected for  $f = 0$  the gap is zero since the transition is continuous.

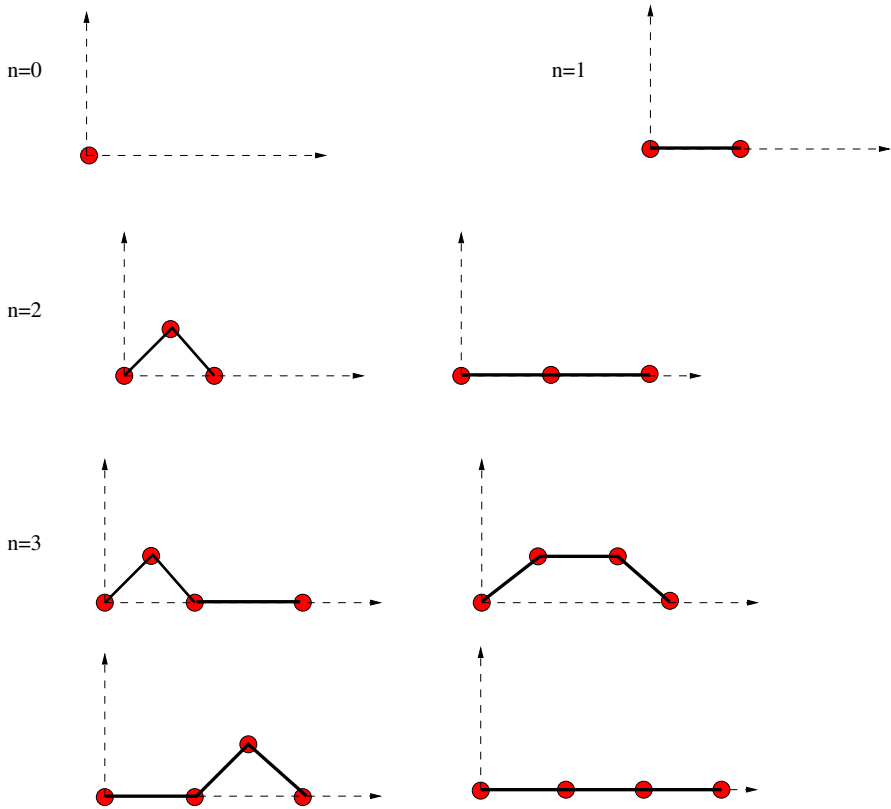
### 3 Walks related to Motzkin paths

Dyck paths have the disadvantage that only alternate vertices can lie in the line  $x_2 = 0$ . Motzkin paths (which differ from Dyck paths by having three kinds of possible step directions  $(1, \pm 1)$  and  $(1, 0)$ ) do not have this disadvantage since they can lie entirely in the line  $x_2 = 0$ . If we write  $m_n$  for the number of Motzkin paths with  $n$  edges then  $m_1 = 1, m_2 = 2, m_3 = 4$  and so on (see Fig. 10). Let

$$M(z) = 1 + \sum_{n \geq 1} m_n z^n \quad (14)$$

be the generating function of the numbers of Motzkin paths, where  $z$  is conjugate to the number of edges,  $n$ . By a factorization argument (similar to the one for Dyck paths),  $M(z)$  satisfies the equation

$$M(z) = (1 + z + z^2 + \dots) \left[ 1 + z^2 M(z)^2 \right] = \frac{1}{1-z} \left[ 1 + z^2 M(z)^2 \right] \quad (15)$$



**Fig. 10** Examples of Motzkin paths for the smallest values of  $n$

so that

$$M(z) = \frac{1 - z - \sqrt{1 - 2z - 3z^2}}{2z^2}. \tag{16}$$

$M(z)$  has a singularity on the positive real axis at  $z = 1/3$  which corresponds to the fact that, for sufficiently large  $n$ , there are about  $3^n$  Motzkin paths, i.e.  $\lim_{n \rightarrow \infty} m_n^{1/n} = 3$ . Similarly to adsorbing Dyck paths we define  $m_n(v)$  to be the number of Motzkin paths with  $n$  edges and  $v + 1$  visits. A similar factorization argument to that leading to (6) implies that the generating function

$$M(x, z) = \sum_{v,n} m_n(v) x^v z^n \tag{17}$$

satisfies the relation

$$\begin{aligned} M(x, z) &= (1 + xz + x^2z^2 + \dots)(1 + xz^2M(1, z)M(x, z)) \\ &= \frac{1 + xz^2M(1, z)M(x, z)}{1 - xz}. \end{aligned} \quad (18)$$

Since  $M(1, z) = M(z)$  we finally get

$$M(x, z) = \frac{1}{1 - zx - \frac{1}{2}x(-z + 1 - \sqrt{-3z^2 - 2z + 1})}. \quad (19)$$

By exploiting the singularity structure of (19) one confirms the scenario found for adsorbing Dyck paths, namely an adsorption transition (at  $x_c = 3/2$ ) between a desorbed phase where the fraction of visits is zero and an adsorbed phase where this fraction is positive. Similarly to Dyck paths the transition is continuous with a cross-over exponent  $\phi = 1/2$ . The main difference with respect to Dyck paths is that, in the ground state limit (i.e.  $T \rightarrow 0^+$ ), the fraction of visits tends to 1. This reflects the fact that there exists a Motzkin path with all vertices lying in the line  $x_2 = 0$ . By relaxing the condition that the last vertex has zero  $x_2$  coordinate we can generalize the Motzkin path description for adsorbing walks to include the action of an elongational force. Similarly to Dyck paths we define  $c_n(v, h)$  as the number of Motzkin paths with  $n$  edges,  $v + 1$  vertices in  $x_2 = 0$ , and whose last vertex has  $x_2$ -coordinate equal to  $h$ . Again, a factorization argument shows that the corresponding generating function

$$C(x, y, z) = \sum_{v, h, n} c_n(v, h)x^v y^h z^n \quad (20)$$

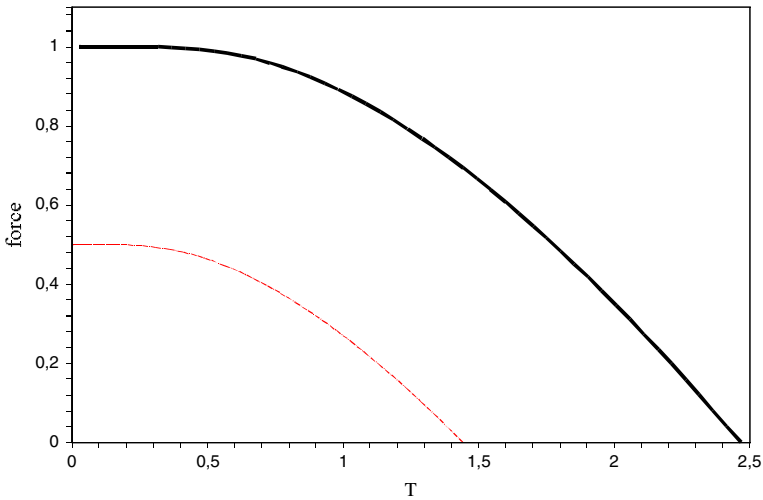
satisfies the relation

$$C(x, y, z) = M(x, z)[1 + yzC(1, y, z)]. \quad (21)$$

By solving Eq. 21 first for  $C(1, y, z)$  (knowing  $M(x, z)$  from (19)) we get

$$C(x, y, z) = \frac{4z}{(2 - zx - x + xu)(2z + yz - y + yu)} \quad (22)$$

where  $u = \sqrt{1 - 2z - 3z^2}$ . This expression for  $C(x, y, z)$  has a square root singularity  $z_d = z_1 = 1/3$  corresponding to the desorbed phase, and two singularities where the denominator is zero. Proceeding as for Dyck paths, we look for the values of  $x$  and  $y$  where the two singularities coincide and this gives the phase boundary in the  $(x, y)$ -plane. Making the substitutions  $y = e^{f/T}$  and  $x = e^{1/T}$  we get the phase diagram in the  $(f, T)$ -plane shown in Fig. 11 [20]. As for Dyck paths the force is a monotone-decreasing function of the the temperature and, for  $T \rightarrow 0$ ,  $f \rightarrow 1$  with zero slope. This is different from the limiting value  $1/2$  found for Dyck paths. This again reflects the fact that while Dyck paths can have at most half of the vertices in the line  $x_2 = 0$ , there exist a Motzkin path with all the vertices on that line. Again,



**Fig. 11** Force–temperature phase diagram for walks related to Motzkin paths (solid line). The thinner (bottom) line is the corresponding phase diagram for Dyck paths (see Fig. 6)

when  $f > 0$  the temperature dependence of the fraction of visits presents a finite discontinuity at  $T = T_c(f)$  confirming that the nature of the adsorption transition changes from continuous to first order when a force is applied.

#### 4 Partially directed walks in three dimensions

Both models considered in the previous sections have phase diagrams in which the force is monotone in the temperature. On the other hand non-monotonic (reentrant) phase diagrams have been seen in directed models of the mechanical denaturation of DNA, i.e. DNA denaturation induced by an applied force [10, 11]. It is then natural to look at other directed models that can reproduce similar features also for the problem of polymer adsorption in presence of an applied force. A successful candidate turned out to be the partially directed walk model in three dimensions [20].

The model which we consider is a self-avoiding walk in  $Z^3$  with coordinates  $(x_1, x_2, x_3)$  and the following constraints:

1. The walk starts at the origin and is confined to the half-space  $x_3 \geq 0$ .
2. The walk has no steps in the negative  $x_1$  and negative  $x_2$  directions.

In analogy with Dyck and Motzkin paths we first consider the pure adsorption problem by looking at the subset of partially directed walks having their last vertex in the plane  $x_3 = 0$ . If we write  $g_n(v)$  for the number of such walks with  $n$  edges and with  $v + 1$  vertices in  $x_3 = 0$ , one can define the corresponding generating function

$$G(x, z) = \sum_{v,n} g_n(v)x^v z^n. \tag{23}$$

A factorization property holds also for partially directed walks giving the recurrence relation

$$G(x, z) = (1 + 2xz + 4x^2z^2 + \dots + 2^p x^p z^p + \dots) \times \left[ 1 + xz^2(G(1, z) - 1) + 2x^2z^3(G(1, z) - 1)G(x, z) \right] \quad (24)$$

which can be written as

$$G(x, z) = \frac{1 + (G(1, z) - 1)xz^2}{1 - 2xz - 2x^2z^3(G(1, z) - 1)}. \quad (25)$$

By putting  $x = 1$  in (25) an explicit expression for  $G(1, z)$  can be found. This gives

$$G(1, z) = \frac{2z^3 - z^2 - 2z + 1 - q}{4z^3} \quad (26)$$

where

$$q = \sqrt{(2z^3 - z^2 - 2z + 1)^2 - 8z^3(1 - z^2)}. \quad (27)$$

$G(x, z)$  is then obtained by plugging expression (26) back to Eq. 25. Clearly  $G(x, z)$  has a square root singularity given by  $q = 0$ , i.e.

$$z_1 = (\sqrt{17} - 3)/4. \quad (28)$$

In addition  $G$  has a set of singularities,  $z_2(x)$ , corresponding to its denominator being zero i.e. when

$$2 - x^2 - 4xz + 2x^2z + x^2z^2 + 2x^2z^3 + x^2q = 0. \quad (29)$$

Equation (29) is a quartic equation whose solutions, that can be found explicitly, are too cumbersome to be reported here. On the other hand by solving the equation  $z_2(x) = z_1$  with respect to  $x$ , i.e. by looking at the point at which the two singularities coalesce one obtains

$$\begin{aligned} (x_c, z(x_c)) &= \left( \frac{3 - 3\sqrt{3} + \sqrt{17}(\sqrt{3} - 1)}{13 - 3\sqrt{17}}, \frac{\sqrt{17} - 3}{4} \right) \\ &= (1.3036\dots, 0.2807\dots). \end{aligned} \quad (30)$$

This corresponds to the location of the adsorption transition for partially directed walks in the absence of an applied force.

In order to include a force term we allow the walks to have their last vertex with  $x_3$ -coordinate not equal to zero. Let  $w_n(v, h)$  be the number of such walks with  $n$

edges,  $v + 1$  vertices in  $x_3 = 0$  and with the  $x_3$ -coordinate of the last vertex equal to  $h$ . Define the generating function

$$W(x, y, z) = \sum_{v,h,n} w_n(v, h)x^v y^h z^n. \tag{31}$$

In order to compute  $W$  it is convenient to consider the subset of walks contributing to  $G$  characterized by having their last edge in the plane  $x_3 = 0$ . We define  $Q(x, z)$  to be the generating function of this subset. Then by a factorization argument we can write

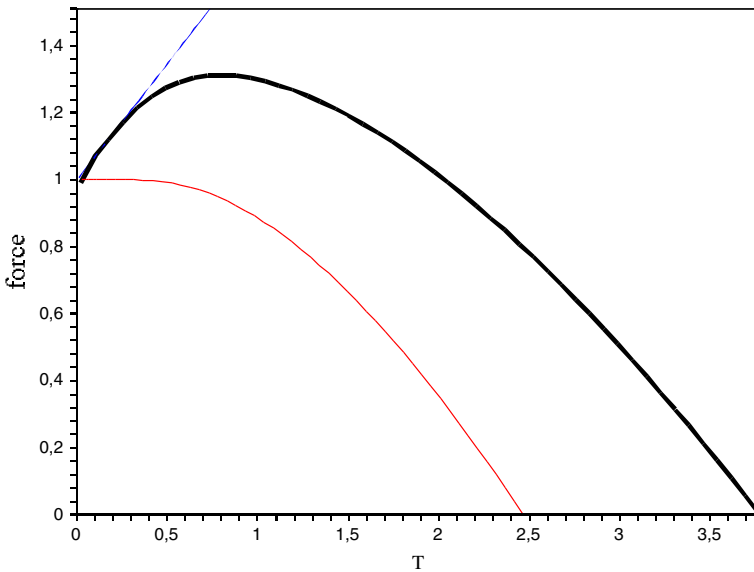
$$Q(x, z) = (1 + 2xz + \dots + 2^p x^p z^p + \dots) \left(1 + 2x^2 z \mathcal{L}(z) Q(x, z)\right) \tag{32}$$

where  $\mathcal{L}(z) = z^2[G(1, z) - 1]$  is the generating function for walks with only the two vertices of degree 1 in  $x_3 = 0$  (partially directed loops). This gives

$$Q(x, z) = \frac{1}{1 - 2xz - 2x^2 z \mathcal{L}(z)}. \tag{33}$$

Then  $W$  is given by the equation

$$W(x, y, z) = G(x, z) + yzQ(x, z)W(1, y, z), \tag{34}$$



**Fig. 12** Force–temperature phase diagram for partially directed walks in three dimensions (solid black curve). The thinner bottom curve refers to the phase diagram for the Motzkin path model. The dotted line corresponds to the low  $T$  approximation  $f_c(T) = 1 + T \log 2$

where the first term on the right-hand side comes from walks ending in  $x_3 = 0$  and the second term is from walks leaving the surface to end in a half-space walk (or tail). By substituting  $x = 1$  we obtain an explicit expression for  $W(1, y, z)$  and hence an expression for  $W(x, y, z)$ .  $W$  is singular when  $z = z^*$  and when the denominator of  $W$  is zero. The denominator factors and we have two possible sets of zeros. The first one is given by the solution of Eq. 29 and it has been discussed previously. The second one is given by the solution

$$1 - 2z - 2yz + z^2 + 2z^3 + q = 0 \quad (35)$$

where  $q$  is given by (27). By defining  $z_3(y)$  to be a real positive root of (35), the phase boundary in the  $(x, y)$ -plane is obtained as the solution of the equation  $z_2(x) = z_3(y)$ . With the changes of variable used in the two dimensional case we then obtain the phase boundary in the  $(T, f)$ -plane, shown in Fig. 12. When  $f = 0$  we have the usual adsorption transition at  $T_c(0) = 1/\log x_c \approx 1/\log(1.3036)$ .

We note that the force goes through a maximum as the temperature varies so the phase diagram is reentrant. We return to this point in the next section.

## 5 Low temperature behaviour and the reentrant transition

One can try to understand the difference between the Dyck-Motzkin models and the partially directed model by looking at the low temperature behaviour of the various force–temperature curves. This can be done by constructing an approximate theory that is either exact in the  $T \rightarrow 0$  limit or gives a fair approximation in this regime [9, 11, 20]. Suppose that  $T$  is close to zero. One can think of the polymer under the influence of a force  $f$  with  $m$  monomers adsorbed and  $n - m$  monomers which have been pulled out into the bulk. The energy contribution to the free energy are then the following:

1. An elastic energy  $-f(n - m)$  from the part of the polymer extending into the bulk,
2. an energy term  $\epsilon\alpha m$  for the part of the polymer adsorbed at the surface. For  $\epsilon = -1$  the term reduces to  $-\alpha m$ .

The entropy contribution is in principle given by two terms: one from the part of the polymer in the bulk and the other from the part of the polymer at the surface. Since the part of the polymer in the bulk is under tension the entropy associated with it can be ignored. The entropic contribution is then entirely due to the part of the polymer at the surface. If we call  $\log \mu$  the conformational entropy per monomer in the adsorbed state then the free-energy of the  $n$ -mer can be written as

$$F_n = -f(n - m) - \alpha m - mT \log \mu \quad (36)$$

Differentiating with respect to  $m$  and setting the derivative equal to zero gives the critical force  $f_c(T)$  as

$$f_c(T) = \alpha + T \log \mu. \quad (37)$$

If  $f > f_c(T)$  then the free energy is dominated by the case  $m = 0$  (desorbed phase) while if  $f < f_c(T)$  the free energy is dominated by the case  $m = n$  and the polymer is completely adsorbed. For Dyck paths  $\alpha = 1/2$  since only half of the  $m$  monomers can be in the adsorbing line while for Motzkin and partially directed walks  $\alpha = 1$  since there exist configurations with all the  $m$  monomers lying at the surface. From Eq. 37 it is clear that the crucial term is the conformational entropy per monomer  $\log \mu$  in the adsorbed (ground state) phase. For Dyck and Motzkin paths  $\mu = 1$  since there is only one completely adsorbed configuration. Hence  $f_c(0)$  is  $1/2$  and  $1$  for these models while the limiting derivative  $df_c(T)/dT$  is zero (zero slope) in the  $T \rightarrow 0$  limit. On the other hand  $\mu = 2$  for partially directed walks since there are  $2^m$  conformations of these walks (with  $m$  edges) that lies completely in the adsorbing plane. In this case  $f_c(0) = 1$  and, more importantly,  $df_c(T)/dT = \log 2$  i.e. the critical force–temperature curve approaches  $1$  with positive slope ( $f_c(T)$  increases as  $T$  increases). Since for  $f \approx 0$  the critical curve is a decreasing function of  $T$  the above argument suggests a non monotonic behavior of the phase diagram for partially directed walks.

## 6 Random copolymer adsorption

The models discussed in the previous sections can be extended to examine the force required to pull a random copolymer from a surface at which it is adsorbed [18,21]. In its simplest version a random copolymer is a polymer made by a sequence  $\chi$  of two types of monomers,  $A$  and  $B$  that in general interact differently with the surrounding environment. This gives rise to interesting equilibrium properties that, in the last decade, have been the subject of several studies especially for systems which exhibit phase transitions such as collapse [22–24] or adsorption [25–27]. Moreover, since the sequence  $\chi$  of monomers is determined by a stochastic process but, once chosen, it is then fixed, random copolymers are an interesting example of quenched randomness (see for instance [28]). In this respect the appropriate free energy of the system is the quenched average free energy

$$\langle F_n(\chi) \rangle = \langle n^{-1} \log Z_n(\chi) \rangle \quad (38)$$

where the angular brackets denote an average over all monomer sequences [28,29] and  $Z_n(\chi)$  is the partition function of the system for a given monomer sequence  $\chi$ . Unfortunately, even for simple models such as Dyck and Motzkin paths it is not possible to calculate quenched average properties analytically (see for instance [30,31]) and one must rely to resort some approximations [32]. The simplest approximation would be the annealed approximation when the order of the expectation and of the logarithm is reversed, but this approximation does not guarantee that even the lower moments of the distribution of colours are correct. An improved approximation was suggested some year ago by Morita [33]. This can be regarded as a partial annealing with a Lagrange multiplier incorporated to ensure that the mean fraction of vertices “coloured”  $A$  is fixed at the required value. It is known [18] that this gives a first order Morita free energy that for Motzkin paths gives the correct asymptotic slope (i.e. the one expected for the quenched free energy) for the adsorption problem.



Clearly, fixing the first moment of the colouring distribution in the statistics does not ensure that higher order correlations are correct but the Morita scheme is flexible enough to allow further improvements through higher order approximations [32,34]. Here we will restrict ourselves to the first order Morita approximation approach to the random copolymer adsorption problem subject to a force.

As the underlying model for the walk configurations we consider Motzkin paths that have the advantage, over Dyck paths, that they can lie entirely over the adsorbing line. Let us first consider the adsorption problem of a random copolymer. The vertices of a Motzkin path with  $n$  edges are labelled by  $i = 0, 1, 2, \dots, n$ . The monomer sequence of the linear random copolymer is described by a sequence of colours  $\chi = \chi_1, \chi_2, \dots, \chi_n$  where  $\chi_i = 1$  if the  $i$ th vertex is A and zero if it is B. For a given sequence  $\chi$  the energy of a given Motzkin path  $\omega$  is formally given by

$$E(\omega|\chi) = \sum_{i=1}^n \epsilon \Delta_i(\omega) \chi_i \quad (39)$$

where  $\Delta_i(\omega) = 1$  if the  $i$ th vertex of  $\omega$  is at the line  $x_2 = 0$  and zero otherwise. Notice that in these notations the homopolymer case treated in Sect. 3 is obtained by putting all the  $\chi_i$  equal to 1. We choose to sample the colour sequence by a Bernoulli process i.e. the colours  $\chi_i$  are chosen independently, with A being chosen with probability  $p$  and B with probability  $1 - p$ . In order to apply the Morita approximation to the adsorbing Motzkin path model it is useful to keep track not only of the number of visit but also of the number of vertices in the bulk [18,21]. We do that by defining the generating function  $F(u, x, z)$  where  $u$  is conjugate to the number of vertices with  $x_2 > 0$ ,  $x$  is conjugate to the number of visits  $v$  and  $z$  is conjugate to  $n$ . A factorization scheme similar to the one described in Fig. 2 gives

$$F(u, w, z) = \frac{1 + uwz^2 M(uz) F(u, w, z)}{1 - wz} \quad (40)$$

and by inserting the explicit expression (16) for the generating function of Motzkin paths (with  $z$  replaced by  $uz$ ) we get

$$F(u, w, z) = \frac{2u}{2u - uwz - w + w\sqrt{1 - 2uz - 3u^2z^2}}. \quad (41)$$

As we said at the beginning of the section, the Morita approximation consists in performing a partial annealing average (i.e. an average over the colour sequences of the partition function) where the proportion of A is fixed to be  $p$  by the introduction of a Lagrange multiplier in the partition function, namely

$$\langle Z_n(x; L) \rangle = \frac{\sum_{\chi} \sum_{\omega \in \Omega_n} x^{v(\omega|\chi)} L^{[\sum_i \chi_i - np]}}{\sum_{\chi} 1} \quad (42)$$

where  $\omega$  is a Motzkin path in the set  $\Omega_n$  of Motzkin paths with  $n$  edges, and  $v(\omega|\chi)$  is the number of A vertices in  $x_2 = 0$  for walk  $\omega$  given the colouring  $\chi$ . By rearranging

expression (42) we get

$$\langle Z_n(x; L) \rangle = L^{-2np} \sum_{\omega \in \Omega_n} \left( pxL^2 + 1 - p \right)^{v(\omega)} \left( pL^2 + 1 - p \right)^{n-v(\omega)} \tag{43}$$

where  $v(\omega)$  is the number of visits for the Mozkin path  $\omega$ . We note that the generating function  $F(u, w, z)$  may be rewritten as

$$F(u, w, z) = \sum_{n \geq 0} z^n \sum_{\omega \in \Omega_n} w^{v(\omega)} u^{n-v(\omega)} \tag{44}$$

and so by making the following substitutions,

$$\begin{aligned} u &\rightarrow pL^2 + 1 - p \\ w &\rightarrow pxL^2 + 1 - p \\ z &\rightarrow z/L^{2p} \end{aligned} \tag{45}$$

we obtain the generating function  $G(x, z, L)$  corresponding to the partition function defined in Eq. 43, namely

$$G(x, z, L) = F(pL^2 + 1 - p, pxL^2 + 1 - p, z/L^{2p}). \tag{46}$$

The generating function  $G$  has two (positive real) singularities. One is a square root singularity that, for  $p = 1/2$ , becomes

$$z = z_1 = \frac{2L}{3(L^2 + 1)} \tag{47}$$

and the other,  $z = z_2$ , comes from a zero of the denominator of  $G$ . Note that, unlike the homopolymer case, the two singularities describing the phase diagram of copolymer adsorption depend on the Lagrange multiplier  $L$  i.e. on the first moment of the colouring distribution. The Morita condition is equivalent to choose  $L$  such that

$$\left\langle \sum_i \chi_i \right\rangle = pn \tag{48}$$

in the  $n \rightarrow \infty$  limit. This gives an  $L$  that in principle depends on  $x$ , i.e. on the temperature of the system. When  $z_1$  is dominant, we choose  $L$  such that

$$L \frac{\partial(-\log z_1)}{\partial L} = 0 \tag{49}$$

and this implies that  $L = L_1 = 1$ , and  $z_1$  is then  $1/3$ , corresponding to the desorbed phase. When  $z_2$  is dominant the expression found for  $L$ ,  $L = L_2(x)$ , is quite complicated to be given explicitly. Substituting  $L_2(x)$  into  $z_2(x, L)$  gives the boundary of

convergence as a function of  $x$  in the adsorbed phase. The boundary of convergence has a singular point at  $x = x_c = (1 + 2p)/2p$  where we have a switch from  $z_1$  being dominant to  $z_2$  being dominant. This corresponds to the adsorption transition in the first order Morita approximation. Note that also the annealing approximation (obtained as a special case of the first order Morita by fixing  $L = 1$  for any value of  $x$ ) gives the same adsorption point  $x_c$ . This is consistent with the results in [35] showing that the Morita approximation *at any order* does not improve over the annealing approximation as far as the location of the adsorption transition is concerned.

Next we include a force term following the procedure developed in Sect. 3 where we called  $c_n(v, h)$  as the number of  $n$ -edge Motzkin paths with  $v + 1$  vertices in  $x_2 = 0$ , having their last vertex with  $x_2$ -coordinate equal to  $h$ . Keeping track also of the number of vertices in the bulk we can define the generating function

$$H(u, w, y, z) = \sum_{v \geq 0} \sum_{h \geq 0} \sum_n b_n(v, h) u^{n-v} w^v y^h z^n. \quad (50)$$

A factorization argument similar to (21) gives

$$H(u, w, y, z) = F(u, w, z)[1 + uyzC(1, y, uz)], \quad (51)$$

and  $H$  can be written as

$$H(u, w, y, z) = \frac{2u(1 - uz + \sqrt{1 - 2uz - 3u^2z^2})}{d_1 d_2} \quad (52)$$

where

$$d_1 = w + uwz - 2u - w\sqrt{1 - 2uz - 3u^2z^2} \quad (53)$$

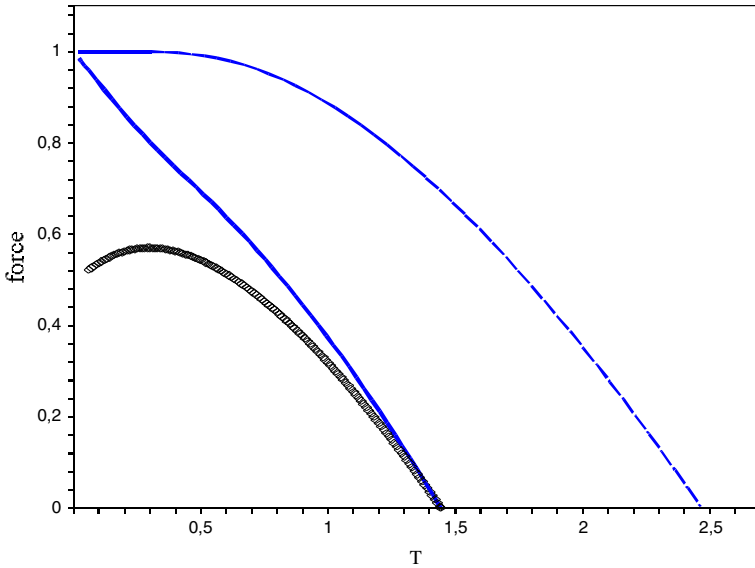
and

$$d_2 = uz - 1 + 2uyz - \sqrt{1 - 2uz - 3u^2z^2}. \quad (54)$$

Clearly  $H(1, x, y, z) = C(w, y, z)$ , i.e. the generating function of the homopolymer model whose phase diagram has been reported in Fig. 11. To determine the critical temperature–force curve in the Morita approximation we make the following substitutions in the generating function  $H(u, w, y, z)$ ,

$$\begin{aligned} u &\rightarrow pL^2 + 1 - p, \\ w &\rightarrow pxL^2 + 1 - p \\ z &\rightarrow z/L^{2p}. \end{aligned} \quad (55)$$

We next determine the singularities of  $H(x, y, z, L)$ . In addition to the square root singularity there are two poles, one given by  $d_1 = 0$  corresponding to the adsorbed phase and the other, solution of the equation  $d_2 = 0$ , corresponding to the phase

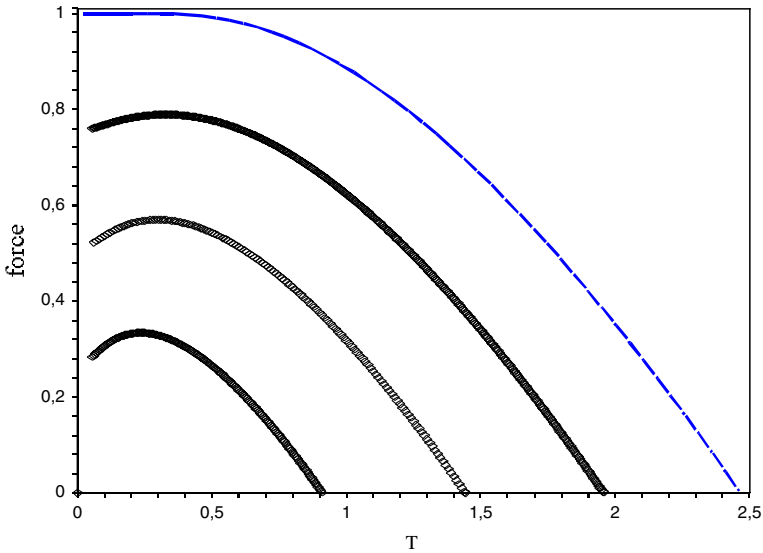


**Fig. 13** The force–temperature diagram for a Motzkin path model of adsorption of a random copolymer at an impenetrable surface, in the presence of a force. The calculation is carried out in the Morita approximation for  $p = 1/2$ . The middle solid curve corresponds to the annealed approximation whereas the top (dotted) curve is for the homopolymer

where the force has caused desorption. The value of  $L$  can be determined in each of these situations (by finding the value of  $L$  such that Eq. 48 is satisfied). The condition of the two singularities being equal gives the critical value of  $y$  as a function of  $x$ ,  $y_c(x)$ . With the substitutions  $x = e^{1/T}$  and  $y = e^{f/T}$  we obtain the Morita approximation of the temperature–force critical curve,  $f_c^{1st}(T|p)$ . In Fig. 13 we compare  $f_c^{1st}(T|1/2)$  with the corresponding curves for the annealed,  $f_c^0(T|1/2)$ , and the homopolymer cases. The most striking result is that, unlike the homopolymer and the annealed cases, the first order Morita approximation for temperature–force curve presents a reentrance. This is true for any value of  $p < 1$  as shown in Fig. 14 for three values of  $p$ . Note that the critical force at  $T = 0$  is  $p$  and that the force goes to zero at  $T = 1/(\log(2p + 1) - \log(2p))$ , which is the location of the adsorption transition in the absence of an applied force.

The presence of a reentrance in the phase diagram of the Morita approximation for the copolymer problem can be explained again in terms of the degeneracy of the ground state ( $T = 0$ ) of the models [21]. At  $T = 0$ , if  $p < 1$ , all the  $A$  vertices of a Motzkin path will be in the surface to minimize the energy. On the other hand the  $B$  vertices can be in or out of the surface since they are neutral with respect to the surface. This gives at least  $2^{(1-p)n}$  configurations of minimal (ground state) energy and the intensive (reduced) entropy  $\mu$  is at least  $(1 - p) \log 2$ . Equation (37) then becomes

$$f_c(T) = p + T \log \mu = p + (1 - p)T \log 2. \tag{56}$$



**Fig. 14** The force–temperature diagram in the Morita approximation for  $p = 1/4$  (bottom),  $p = 1/2$  (second from bottom) and  $p = 3/4$  (third from bottom). The top curve is for the homopolymer

and the force–temperature curve will have a slope (at  $T = 0$ ) at least as large as  $(1 - p) \log 2$ . In Fig. 14 it is clear that this slope at  $T = 0$  decreases as  $p$  increases, as expected from the above rough argument. The value of the critical force at  $T = 0$  for the Motzkin path model is  $p$  since the energy to be overcome is  $pn$ . For the Dyck path model the corresponding value is  $p/2$  since only alternate vertices can be in the surface.

## 7 Discussion

We have shown that directed walk models such as Dyck, Motzkin and partially directed walks can be successfully implemented on a generating function approach to study the problem of polymer adsorption in presence of an elongational force. Indeed by simple combinatorial arguments the analytical expression of the generating functions of these models can be obtained and, by looking at their singularity structure, it is possible to determine the form of the phase boundary in the force–temperature plane, i.e. the temperature dependence of the critical force for desorption. As the temperature goes to zero, the critical force goes to  $1/2$  for the Dyck path model and to  $1$  for the Motzkin path model. This reflects the difference in the ground state energies of the two models. When the applied force is zero the adsorption transition is continuous with crossover exponent equal to  $1/2$ , as found for other directed models of polymer adsorption [16, 19]. If, on the other hand, a positive force is applied the adsorption transition becomes first order implying that the order of the transition changes when a force is applied. Since Dyck and Motzkin paths have only a single configuration with minimal energy, the configurational entropy per monomer in the ground state ( $T = 0$ )

is zero. If one considers instead the partially directed walk model that has a residual specific entropy at  $T = 0$ , a reentrant phase diagram is observed [20]. This reentrance has been confirmed recently by a numerical investigation of the full adsorbing self-avoiding walk model in 3D [36] and can be understood by a simple argument valid at low  $T$  where the entropy in the ground state plays a significant role.

The relative simplicity and flexibility of directed walk models allow the extension of the generating function approach to the problem of a random copolymer adsorption where a force can cause desorption [21]. The copolymer can be modelled by two types of monomers (A and B) where the monomers are distributed independently with the probability that a monomer is A being  $p$ . We show that, within the Motzkin path model, the first order Morita approximation to the quenched problem can be solved exactly for any value of  $p$ . The force-temperatures curves obtained show remarkable richness. In particular for  $0 < p < 1$  the critical force is not a monotonic function of  $T$  but presents a reentrance. This is different either from the homopolymer case or from the annealed approximation (zero order Morita) where the reentrance is not present and is associated to the degeneracy of the ground state of the model introduced by the randomness of the monomer sequence. This shows that the first order Morita approach furnishes a significant improvement over the annealed one in approximating the quenched problem. A problem closely related to the mechanical desorption of random copolymer concerns the influence of disorder in the mechanical unzipping of DNA [37]. In this respect techniques similar to the ones discussed here have been recently implemented to show that the Morita approximation furnishes a good bound on the force required to unzip the DNA in the quenched case [38].

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