Eur. Phys. J. B **40**, 63–71 (2004)
DOI: 10.1140/epjb/e2004-00239-1

**THE EUROPEAN
PHYSICAL JOURNAL B**

Adsorption and localization of random copolymers subject to a force: The Morita approximation

G. Iliev[1], E. Orlandini[2,a], and S.G. Whittington[1]

[1] Department of Chemistry, University of Toronto, Toronto, Canada
[2] INFM, Dipartimento di Fisica, Università di Padova, Via Marzolo 8, 35131 Padova, Italy

Received 18 February 2004 / Received in final form 17 May 2004

Abstract. We discuss directed walk models of random copolymers, either adsorbed at a surface or localized at an interface between two immiscible liquids. We consider the response to an applied force which can cause desorption or delocalization into a bulk phase, and calculate the critical force as a function of temperature. The randomness is quenched and, even for directed models, we cannot usually treat the quenched system analytically so we resort to an approximation in which the quenched average is approximated by an annealed average with a side condition which ensures the correct proportion of the types of comonomers. We argue that this approach gives the exact result for the quenched system in some cases and a bound in others.

PACS. 36.20.Ey Conformation (statistics and dynamics) – 05.70.Jk Critical point phenomena in thermodynamics – 64.60.-i General studies of phase transitions

1 Introduction

Experimental techniques such as atomic force microscopy and optical tweezers have made it possible to micromanipulate single polymer molecules and to measure their response to an applied force (see for instance [1] and [2] and references therein). For instance, it is in principle possible to pull an adsorbed polymer off a surface and measure the free energy change.

There is a large volume of literature on the statistical mechanics of polymer adsorption (see [3] and [4] for reviews) and directed walk models have proved very useful in understanding the adsorption transition [5–8]. In a similar way, there has been considerable interest in localization of a random copolymer at an interface between two immiscible liquids ([9–11] and references therein), and directed walk models have contributed to our understanding of this phenomenon [7,12,13]. Recently Orlandini et al. [14] considered a directed walk model of homopolymer adsorption at an impenetrable surface in which a force was applied to pull the polymer off the surface. They calculated the temperature dependence of the critical force for several different directed walk models and noted that the force was a monotone decreasing function of temperature for some models, while for others the force had a maximum value at some non-zero temperature. The difference is associated with the entropy of the ground state. For systems with a degenerate ground state there is an entropy loss when the polymer is partially pulled off the surface and this leads to a critical force which increases with increasing temperature at low temperature.

Currently there is considerable interest in the statistical mechanics of random copolymers. We shall be concerned with random copolymers which have two types of monomers, A and B. Since the sequence 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 [15]). In this paper we examine (i) the force required to pull a random copolymer from a surface at which it is adsorbed, (ii) the force required to pull a random copolymer from a bulk phase (into which it is delocalized) into a less favourable bulk phase, and (iii) the force required to pull a random copolymer from an interface (at which it is localized) into a bulk phase. We use very simple directed walk models (related to Dyck paths and to Motzkin paths) for the underlying configurational properties of the polymer. Even for these models it is not always possible to calculate quenched average properties analytically (see for instance [12]) and we are obliged to resort to an approximation. The simplest approximation would be the annealed approximation but it is known that this gives a qualitatively incorrect phase diagram for localization [7]. Instead we use an approximation originally suggested by Morita [16]. This can be regarded as a partial annealing in which a Lagrange multiplier is used to ensure that the mean fraction of vertices labelled A is fixed at the required

---

[a] e-mail: `orlandini@pd.infn.it`

value. It is known [7] that this gives a phase diagram for the localization problem which is qualitatively correct, although it differs quantitatively from the quenched values. (For numerical estimates of the phase boundaries for a self-avoiding walk model see James et al. [17]). We argue that the Morita approximation gives the exact result for the required force in some cases, and a bound in others.

2 Adsorption at an impenetrable surface

In this paper we focus on directed walks to model the conformational properties of single polymer chains. The simplest such model of a polymer interacting with an impenetrable surface is a Dyck path. This is a directed walk on the square lattice Z^2 with edges which are vectors $(1, \pm 1)$. If we set up the standard coordinate system so that a vertex of the square lattice has integer coordinates (x_1, x_2), then the walk starts at the origin, has no vertices with $x_2 < 0$, and has its final vertex in the line $x_2 = 0$. If we take the line $x_2 = 0$ to represent the surface at which adsorption can occur, Dyck paths have the disadvantage that only alternate vertices can be in this line. Motzkin paths (which differ from Dyck paths by having three kinds of edges, $(1, \pm 1)$ and $(1, 0)$) do not have this disadvantage since they can lie entirely in the line $x_2 = 0$. We shall analyse two models: one related to Dyck paths with only alternate vertices randomly coloured, and one related to Motzkin paths with all vertices randomly coloured. The Motzkin path case is slightly simpler, and we discuss this case first.

Suppose that c_n is the number of Motzkin paths with n edges. Then $c_1 = 1$, $c_2 = 2$, $c_3 = 4$, $c_4 = 9$, etc. Let $M(z)$ be the generating function of the numbers of Motzkin paths, where z is conjugate to the number of edges, n, so that

$$M(z) = \sum_n c_n z^n. \tag{1}$$

By factoring the Motzkin path at its first return to the axis, $M(z)$ satisfies the equation

$$M(z) = (1 + z + z^2 + \ldots)[1 + z^2 M(z)^2] \tag{2}$$

so that

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

We write $c_n(v)$ for the number of Motzkin paths with n edges and $v+1$ vertices in the line $x_2 = 0$. Suppose the $n+1$ vertices of the Motzkin path are numbered $i = 0, 1, 2, \ldots n$. For a model of homopolymer adsorption the energy of the walk can be defined to be $v\epsilon$ where ϵ is the energy contribution for each vertex $(i \geq 1)$ in the line $x_2 = 0$. That is, the Hamiltonian is given by

$$\mathcal{H}(\omega) = \sum_{i=1}^{n} \epsilon \Delta_i(\omega) \tag{4}$$

where ω is a Motzkin path and $\Delta_i(\omega) = 1$ if the ith vertex of ω is at the surface (line $x_2 = 0$) and zero otherwise. We define $x = \exp[-\epsilon/k_B T]$ where k_B is Boltzmann's constant and T is the temperature. An attractive interaction with the surface corresponds to $\epsilon < 0$, i.e. to $x > 1$. The variable x is conjugate to v and the corresponding generating function

$$\begin{aligned} M(x,z) &= \sum_n \sum_\omega \exp[-\mathcal{H}(\omega)/k_B T] z^n \\ &= \sum_n \sum_{v=0}^{n} c_n(v) x^v z^n \end{aligned} \tag{5}$$

satisfies the equation [14]

$$M(x,z) = (1 + xz + x^2 z^2 + \ldots)[1 + xz^2 M(z) M(x,z)] \tag{6}$$

so that

$$M(x,z) = \frac{2}{2 - x - xz + x\sqrt{1 - 2z - 3z^2}}. \tag{7}$$

$M(x,z)$ has a square root singularity at $z = z_1 = 1/3$ and a pole, corresponding to a zero of the denominator, at

$$z = z_2 = \frac{1 - x + \sqrt{x^2 + 2x - 3}}{2x}. \tag{8}$$

The singularity z_1 corresponds to the desorbed phase and the singularity z_2 to the adsorbed phase. The two singularities coallesce at $x^* = 3/2$ which is the location of the adsorption transition for the homopolymer.

We next examine the adsorption of a random copolymer with two types of monomers, A and B, where only A monomers interact with the adsorbing surface. For a given sequence $\chi = \{\chi_i, i = 1, 2, \ldots n\}$ of monomers the Hamiltonian can be written

$$\mathcal{H}(\omega|\chi) = \sum_{i=1}^{n} \epsilon \Delta_i(\omega) \chi_i \tag{9}$$

where $\chi_i = 1$ if the ith monomer is A and zero if it is B. Notice that the Hamiltonian depends both on the conformation ω and on the monomer sequence χ.

In order to apply the Morita approximation we follow the scheme used in [7]. We first need to count paths keeping track of the number of vertices in $x_2 = 0$ and the number with $x_2 > 0$. We define the generating function $F(u,w,z)$ where u is conjugate to the number of vertices with $x_2 > 0$, w is conjugate to v and z is conjugate to n. A similar factorization scheme gives

$$F(u,w,z) = \frac{1 + uwz^2 M(uz) F(u,w,z)}{1 - wz} \tag{10}$$

so that

$$F = \frac{2u}{2u - uwz - w + w\sqrt{1 - 2uz - 3u^2 z^2}}. \tag{11}$$

Suppose that the vertices of the Motzkin path are numbered $i = 0, 1, 2, \ldots n$ and suppose the vertices $1, 2, \ldots n$ are independently coloured A with probability p and B

with probability $1-p$. We write $\chi_i = 1$ if the ith vertex is coloured A and $\chi_i = 0$ if it is coloured B, and note that the χ_i are independent random variables. We now introduce a variable L which plays the role of a Lagrange multiplier, to ensure that the mean fraction of vertices labelled A is fixed at p. In fact we shall give the details only for the choice $p = 1/2$, but extension to other values of p is straightforward. We write

$$\langle Z_n(x;L)\rangle = \frac{\sum_\chi \sum_{\omega\in\Omega_n} x^{v(\omega|\chi)} L^{[2\sum_i \chi_i - n]}}{\sum_\chi 1} \tag{12}$$

where ω is a Motzkin path in the set Ω_n of Motzkin paths with n edges, and $v(\omega|\chi)$ is the number of A vertices in $x_2 = 0$ for walk ω given the colouring χ. This expression can be rearranged to give

$$\langle Z_n(x;L)\rangle = L^{-n} \sum_{\omega\in\Omega_n} \left(\frac{xL^2+1}{2}\right)^{v(\omega)} \left(\frac{L^2+1}{2}\right)^{n-v(\omega)} \tag{13}$$

where $v(\omega)$ is the number of visits to $x_2 = 0$ for walk ω. We observe that the generating function F can be written as

$$F(u,w,z) = \sum_{n\geq 0} z^n \sum_{\omega\in\Omega_n} w^{v(\omega)} u^{n-v(\omega)}. \tag{14}$$

Let

$$G(x,z;L) = \sum_n \langle Z_n(x;L)\rangle z^n \tag{15}$$

be the generating function of the random copolymer in the Morita approximation (with L yet to be determined). We make the substitutions $u \to (L^2+1)/2$, $w \to (xL^2+1)/2$ and $z \to z/L$ in the expression for F, giving

$$G(x,z,L) = F((L^2+1)/2, (xL^2+1)/2, z/L). \tag{16}$$

The generating function G has two (positive real) singularities. One is a square root singularity at

$$z = z_1 = \frac{2L}{3(L^2+1)} \tag{17}$$

and the other, $z = z_2$, comes from a zero of the denominator of G. We now determine the value of L (which in general depends on x) by choosing L such that

$$\left\langle \sum_i \chi_i \right\rangle = n/2 \tag{18}$$

in the $n \to \infty$ limit. Ie, when z_1 is dominant, we choose L such that

$$L\frac{\partial(-\log z_1)}{\partial L} = 0 \tag{19}$$

and this implies that $L = L_1 = 1$ when z_1 is dominant, and z_1 is then $1/3$, corresponding to the desorbed phase. When z_2 is dominant we follow a similar procedure and find a complicated expression for L, $L = L_2(x)$. Substituting this into z_2 gives the boundary of convergence as a function of x in the adsorbed phase. The boundary of convergence has a singular point at $x = 2$ where we have a switch from z_1 being dominant to z_2 being dominant. This corresponds to the adsorption transition in this approximation.

Next we include a force term f. The Hamiltonian (9) generalizes now to

$$\mathcal{H}(\omega, f|\chi) = \sum_{i=1}^{n} \epsilon \Delta_i(\omega)\chi_i - fh \tag{20}$$

where h is the x_2 coordinate of the final vertex of the walk (*final height*). (Note that the case $h = 0$ corresponds to Motzkin paths interacting with the surface). Suppose that the number of such n-edge walks with $v+1$ vertices in $x_2 = 0$, having final height equal to h, is $b_n(v,h)$. As in the case of zero force, the Morita approximation can be computed by defining the generating function

$$H(u,w,y,z) = \sum_{v\geq 0}\sum_{h\geq 0}\sum_n b_n(v,h) u^{n-v} w^v y^h z^n. \tag{21}$$

that also takes into account the number of vertices $n-v$ with $x_2 > 0$. Let $M_1(y,z) = H(1,1,y,z)$. By a factorization argument M_1 satisfies the relation

$$M_1(y,z) = F(1,1,z)[1 + yzM_1(y,z)] \tag{22}$$

so that

$$M_1 = \frac{2}{1 - z - 2yz + \sqrt{1-2z-3z^2}}. \tag{23}$$

Then

$$H(u,w,y,z) = F(u,w,z)[1 + uyzM_1(y,uz)], \tag{24}$$

and H can be written as

$$H = \frac{2u(1 - uz + \sqrt{1-2uz-3u^2z^2}}{d_1 d_2} \tag{25}$$

where

$$d_1 = w + uwz - 2u - w\sqrt{1-2uz-3u^2z^2} \tag{26}$$

and

$$d_2 = uz - 1 + 2uyz - \sqrt{1-2uz-3u^2z^2}. \tag{27}$$

Setting $u = 1$ and $w = x$ gives the homopolymer model. $H(1,x,y,z)$ has a square root singularity but also singularities corresponding to $d_1 = 0$ and to $d_2 = 0$. The zero of d_1 corresponds to the adsorbed phase and the zero of d_2 to the phase in which the applied force dominates. Equating these two singularities gives the critical value of y as a function of x and making the substitutions $y = e^{f/T}$ and $x = e^{1/T}$ gives the temperature dependence of the critical force, f. This reproduces the results in Figure 2 in [14].

To determine the force in the Morita approximation we make the substitutions $u \to (L^2+1)/2$, $w \to (xL^2+1)/2$ and $z \to z/L$ in the expression for H. We then determine the singularities of H and identify the singularity

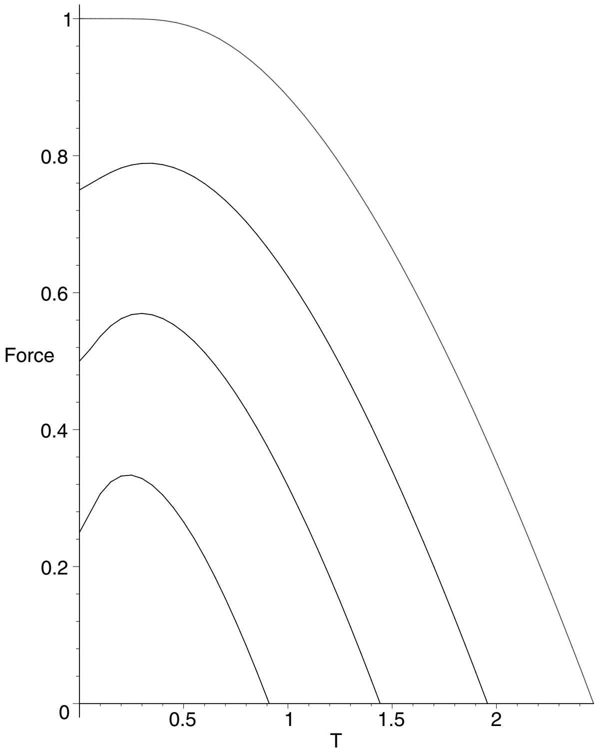

Fig. 1. The force-temperature diagram for a Motzkin path model of adsorption of a random copolymer at an impenetrable surface, in the presence of a force. The calculation is carried out in the Morita approximation. The lower three curves are for $p = 1/4$ (bottom curve), $p = 1/2$ and $p = 3/4$. The top curve is for the homopolymer.

$z = z_1^M(L)$ (where $d_1 = 0$) corresponding to the adsorbed phase and the singularity $z = z_2^M(L)$ (where $d_2 = 0$) corresponding to the phase 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 $\langle \sum \chi_i \rangle = n/2$), and we find that

$$z_2^M = y/(1 + y + y^2). \tag{28}$$

Equating the two singularities gives the critical value of y as a function of x. The above substitutions, to incorporate force and temperature, then give the results shown in Figure 1 for the temperature dependence of the critical force needed for desorption for $p = 1/4$ (bottom curve), $p = 1/2$, $p = 3/4$ and for the homopolymer ($p = 1$, top curve). The critical force at $T = 0$ is p and 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. For $p < 1$ the critical force goes through a maximum so the phase diagram is reentrant, unlike the homopolymer phase diagram. We shall return to this point in Section 4.

The Morita treatment is not only an approximation to the quenched problem but gives a bound on the force required for the quenched problem, as we now discuss. The quenched average free energy with final vertex at $x_2 = h$ is given by

$$\bar{\kappa}(x, h) = \lim_{n\to\infty} \langle n^{-1} \log Q_n(x, h|\chi)\rangle \tag{29}$$

where the partition function $Q_n(x, h|\chi)$ is given by

$$\begin{aligned} Q_n(x, h|\chi) &= \sum_{\{\omega|h\}} \exp[-\mathcal{H}(\omega|\chi)/k_B T] \\ &= \sum_{v_A} b_n(v_A, h|\chi) x^{v_A} \end{aligned} \tag{30}$$

where the first sum runs over the set $\{\omega|h\}$, the set of n-edge walks with their last vertex in $x_2 = h$, and $b_n(v_A, h|\chi)$ is the number of n-edge walks with final height h and with v_A A-vertices in $x_2 = 0$, given χ.

Suppose that $x \leq 1$. Then

$$\begin{aligned} t_n(h) \leq b_n(0, h|\chi) &\leq Q_n(x, h|\chi) \\ &\leq \sum_{v_A} b_n(v_A|\chi) = b_n(h), \end{aligned} \tag{31}$$

independent of χ, where $b_n(h)$ is the number of n-edge walks with final height h and $t_n(h)$ is the number of n-edge walks having final height h and with only the zeroth vertex in $x_2 = 0$. Now

$$b_n(h) = t_{n+1}(h + 1). \tag{32}$$

Multiplying by $y^h z^n$ and summing over n and h gives

$$\begin{aligned} \sum_n \sum_h t_n(h) y^h z^n &\leq \sum_n \sum_h Q_n(x, h|\chi) y^h z^n \\ &\leq \sum_n \sum_h t_{n+1}(h + 1) y^h z^n, \end{aligned} \tag{33}$$

so the large n behaviour of the generating function

$$\hat{Q}_n(x, y|\chi) = \sum_h Q_n(x, h|\chi) y^h, \tag{34}$$

when $x \leq 1$, is determined by the boundary of convergence of the generating function

$$T(y, z) = \sum_n \sum_h t_n(h) y^h z^n, \tag{35}$$

i.e. by

$$z = z_c = y/(1 + y + y^2). \tag{36}$$

This is precisely the value of z_2^M, the zero of d_2, so the free energy in the Morita approximation is exactly equal to the quenched average free energy when $x \leq 1$ and, since this value is independent of x, for all values of x corresponding to desorption. By a result due to Kühn [18], the quenched average free energy in the adsorbed phase is bounded by the Morita approximation to the free energy, i.e. by the free energy related to the zero of d_1. This implies that the value of z_1 for the quenched case, z_1^Q, is related to z_1^M by the inequality $z_1^Q \geq z_1^M$. At fixed x, z_2^M decreases as y increases and becomes equal to z_1^Q at a critical value

$y = y_c^Q(x)$ and to z_1^M at a critical value $y = y_c^M(x)$. This latter value determines the critical force in the Morita approximation. Since $z_1^Q \geq z_1^M$, $y_c^Q(x) \leq y_c^M(x)$. Hence the force required for desorption in the quenched case is less than or equal to that in the Morita approximation.

We next compare these results to those obtained for a Dyck path model. If the vertices of the Dyck path are labelled $i = 0, 1, \ldots n$ (with n even) then only the vertices $0, 2, 4, \ldots n$ can be in the line $x_2 = 0$. If we colour all vertices A or B then Orlandini et al. showed [7] that the Morita approximation does very badly at low temperatures since the behaviour is dominated by the colouring in which the even vertices are coloured A and the odd vertices are coloured B (so that half the vertices have each colour but the correlations are completely wrong). This problem can be circumvented by colouring only even vertices ($i = 2, 4, \ldots n$) and leaving the remaining vertices uncoloured (since the odd vertices can not lie in $x_2 = 0$).

We first count Dyck paths. If $D(z)$ is the generating function of Dyck paths with z conjugate to the number of edges n then $D(z)$ satisfies the relation

$$D(z) = 1 + z^2 D(z)^2 \tag{37}$$

so that

$$D(z) = \frac{1 - \sqrt{1 - 4z^2}}{2z^2}. \tag{38}$$

We shall need to keep track of the number of Dyck paths with a given number of odd vertices, so let $D_o(v, z)$ be the corresponding generating function where v is conjugate to the number of odd vertices. Then

$$D_o(v, z) = \frac{1 - \sqrt{1 - 4vz^2}}{2vz^2}. \tag{39}$$

If D_e is the corresponding generating function where v is conjugate to the number of even vertices (not counting the zeroth vertex) then $D_e = D_o$. Define the generating function $F_e(u, w, z)$ which counts Dyck paths where u is conjugate to the number of even vertices with $x_2 > 0$, w is conjugate to the number of even vertices in $x_2 = 0$ and z is conjugate to the number of edges. F_e satisfies

$$F_e(u, w, z) = 1 + wz^2 D_o(u, z) F_e(u, w, z) \tag{40}$$

so that

$$F_e(u, w, z) = \frac{2u}{2u - w + w\sqrt{1 - 4uz^2}}. \tag{41}$$

Setting $u = 1$ and $w = x$ gives the homopolymer generating function for this model, studied in [7]. For the Morita approximation we make the substitutions $u \to (L^2 + 1)/2$, $w \to (xL^2 + 1)/2$ and $z \to z/\sqrt{L}$ (recall that only half the vertices are coloured). This is equivalent to the treatment in [7] and gives an adsorption transition at $x = x_c = 3$, which is the same as for the annealed model. However, the number of A vertices in $x_2 = 0$, per edge of the Dyck path, goes to $1/4$ as the temperature goes to zero, as expected for the quenched system.

To introduce a force we count the corresponding paths with their last vertex in $x_2 = h$. Let $H_e(u, w, y, z)$ count such paths where u is conjugate to the number of even vertices with $x_2 > 0$, w is conjugate to the number of even vertices with $x_2 = 0$, y is conjugate to h and z is conjugate to the number of edges, n, and let $H_o(u, y, z)$ count the paths where u is conjugate to the number of odd vertices (each of which has $x_2 > 0$). Let $F_o(u, z)$ count Dyck paths where u is conjugate to the number of odd vertices. Then factorization arguments show that $H_e(u, 1, y, z)$ and $H_o(u, y, z)$ are related by the simultaneous equations

$$H_e(u, 1, y, z) = F_e(u, 1, z)[1 + yzH_o(u, y, z)], \tag{42}$$

$$H_o(u, y, z) = F_o(u, z)[1 + uyzH_e(u, 1, y, z)] \tag{43}$$

and that

$$H_e(u, w, y, z) = F_e(u, w, z)[1 + yzH_o(u, y, z)]. \tag{44}$$

Noting that

$$F_o(u, z) = 1 + uz^2 D_e(u, z) F_o(u, z) \tag{45}$$

we can solve the above equations for $H_e(u, w, y, z)$. This gives

$$H_e(u, w, y, z) = \frac{2[(u + yz)\sqrt{q_0} + u - yz - 2uz^2 - 2uyz]}{q_1 q_2}, \tag{46}$$

where $q_0 = 1 - 4uz^2$, $q_1 = 2u - w + w\sqrt{1 - 4uz^2}$ and $q_2 = 1 + \sqrt{1 - 4uz^2} - 2z^2 - 2uy^2z^2$. Making the above substitutions for the Morita approximation, identifying the singularities of H_e, determining L in the different regimes, and equating the two singularities coming from the denominator of H_e, we find the x-dependence of y. With the substitutions $x = e^{1/T}$ and $y = e^{f/T}$ this gives the temperature dependence of the critical force, and this is shown in Figure 2.

Note that the force goes to zero when $T = 1/\log 3$ (corresponding to $x_c = 3$) and is equal to $1/4$ when $T = 0$. Note also that the force goes through a maximum value for a non-zero value of the temperature, as found for the Motzkin path model. An argument similar to that given for the Motzkin path model establishes that the critical force in the Morita approximation is an upper bound on the required force for the quenched case.

3 Localization at an interface between two immiscible liquids

In this section we consider two immiscible liquids α and β and a random copolymer with two types of monomers A and B which have different energy contributions in the two liquid phases. Depending on the conditions the polymer can be delocalized into one liquid phase or localized at the interface between the two bulk phases. This problem has been extensively studied in the absence of a force and the form of the phase diagram (for a Dyck path model) is well understood [12]. We examine two situations when

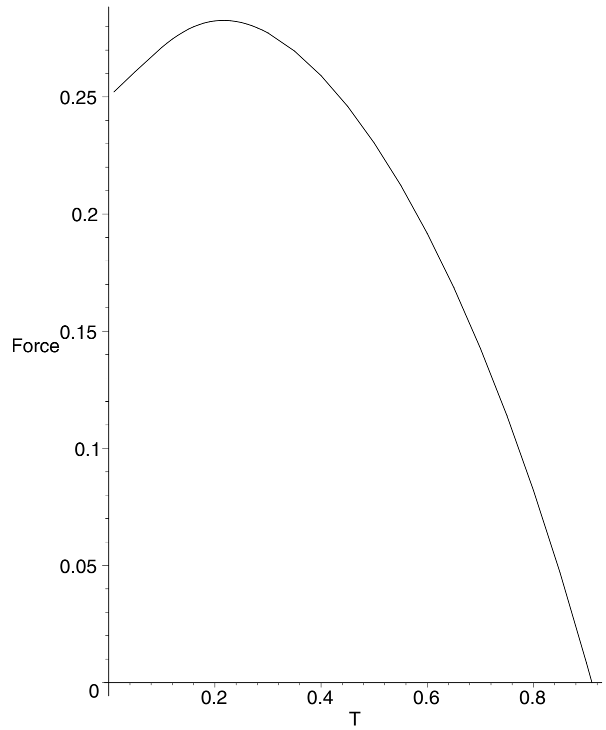

Fig. 2. The force-temperature diagram for a Dyck path model of adsorption of a random copolymer at an impenetrable surface, in the presence of a force. The calculation is carried out in the Morita approximation and $p = 1/2$.

a force is applied. We first consider the situation where the copolymer is delocalized into one liquid phase and is then pulled into the less favourable liquid phase. We also consider the case where the copolymer is localized at the interface and is then pulled into one of the bulk phases.

The model that we use is essentially that considered in [7]. They considered bilateral Dyck paths, i.e. directed walks with edges along the directions $(1, \pm 1)$, which start at the origin and have their last vertex in the line $x_2 = 0$. The vertices are numbered $i = 0, 1, 2, \ldots n$ and vertices $1, 2, \ldots n$ are independently coloured A with probability p and B with probability $1 - p$. We write $\chi_i = 1$ if the ith vertex is A and 0 if it is B. For a given a colouring sequence $\chi = \{\chi_1, \chi_2, \ldots \chi_n\}$ the Hamiltonian of the model is given by

$$\mathcal{H}(\omega, |\chi) = \sum_{i=1}^{n} \left(\epsilon_A \chi_i \Delta_i^+(\omega) + \epsilon_B (1 - \chi_i) \Delta_i^-(\omega) \right) \quad (47)$$

where $\Delta_i^+ = 1$ if the i'th vertex has positive x_2-coordinate and zero otherwise, and $\Delta_i^- = 1$ if the i'th vertex has negative x_2-coordinate and zero otherwise. ϵ_A and ϵ_B are the energies associated with an A monomer being in the α-phase ($x_2 > 0$) and with a B monomer being in the β-phase ($x_2 < 0$). Let $b_n(v_A, v_B|\chi)$ be the number of bilateral Dyck paths, given a colouring sequence χ with v_A A-vertices with $x_2 > 0$ (the α-phase) and v_B B-vertices with $x_2 < 0$ (the β-phase). The partition function is

$$Z_n(a, b|\chi) = \sum_{\omega} \exp\left[-\mathcal{H}(\omega, |\chi)/k_B T\right] \quad (48)$$

$$= \sum_{v_A, v_B} b_n(v_A, v_B|\chi) a^{v_A} b^{v_B} \quad (49)$$

where $a = \exp[-\epsilon_A/k_B T]$ and $b = \exp[-\epsilon_B/k_B T]$.

In the Morita approximation one introduces an additional term, which plays the role of a Lagrange multiplier, giving

$$\langle Z_n(a, b|\chi) \rangle = \frac{\sum_{\chi, v_A, v_B} b_n(v_A, v_B|\chi) a^{v_A} b^{v_B} L^{[2\sum_i \chi_i - n]}}{\sum_{\chi} 1} \quad (50)$$

which, when $p = 1/2$, can be rewritten as

$$\langle Z_n(a, b|\chi) \rangle = L^{-n} \sum_{\omega \in \Omega_n} U^{u(\omega)} V^{v(\omega)} W^{w(\omega)} \quad (51)$$

where u, v and w are the numbers of vertices with $x_2 > 0$, $x_2 < 0$ and $x_2 = 0$, respectively and U, V and W are given by

$$U = \left(\frac{aL^2 + 1}{2} \right), \quad V = \left(\frac{L^2 + b}{2} \right) \quad (52)$$

and

$$W = \left(\frac{L^2 + 1}{2} \right). \quad (53)$$

We first count bilateral Dyck paths. Let $B(a, b, c, z)$ be the generating function of bilateral Dyck paths, where a is conjugate to the number of vertices with $x_2 > 0$, b is conjugate to the number of vertices with $x_2 < 0$ and c is conjugate to the number of vertices with $x_2 = 0$, not counting the zeroth vertex. Also, z is conjugate to the number of edges. The generating function B satisfies the relation

$$B(a, b, c, z) = 1 + cz^2 B(a, b, c, z)[aD(az) + bD(bz)] \quad (54)$$

so that

$$B(a, b, c, z) = \frac{2ab}{2ab - ac - bc + acb_1 + bca_1}, \quad (55)$$

where $a_1 = \sqrt{1 - 4a^2 z^2}$ and $b_1 = \sqrt{1 - 4b^2 z^2}$. We can construct the Morita approximation (for $p = 1/2$) by making the substitutions $a \to (aL^2 + 1)/2$, $b \to (L^2 + b)/2$, $c \to (L^2 + 1)/2$ and $z \to z/L$. The generating function $B((aL^2 + 1)/2, (L^2 + b)/2, (L^2 + 1)/2, z/L)$ has two square root singularities

$$z_1 = \frac{L}{aL^2 + 1} \quad (56)$$

and

$$z_2 = \frac{L}{L^2 + b} \quad (57)$$

and a third singularity corresponding to a zero of the denominator of B. The value of L required to ensure that

$\langle\sum_i \chi_i\rangle = n/2$ in the $n \to \infty$ limit depends on the values of a and b. When z_1 is dominant, $L = L_1 = 1/\sqrt{a}$, which gives $z_1 = 1/(2\sqrt{a})$. This corresponds to delocalization into the α-phase, $x_2 > 0$. Similarly, when z_2 is dominant, $L = L_2 = \sqrt{b}$, giving $z_2 = 1/(2\sqrt{b})$, which corresponds to delocalization into the β-phase, $x_2 < 0$.

To introduce a force we count the corresponding walks which end in the line $x_2 = h$. Let $Q(a,b,c,y,z)$ be the corresponding generating function where y is conjugate to h and the other symbols have the same meaning as in the definition of B. Then Q satisfies the relation

$$Q(a,b,c,y,z) = B(a,b,c,z)[1 + ayzD_1(y,az)] \qquad (58)$$

where

$$D_1(y,z) = D(z)[1 + yzD_1(y,z)]. \qquad (59)$$

Hence

$$Q = \frac{4a^2bz}{g_1g_2} \qquad (60)$$

where $g_1 = 2ab - ac - bc + ac\sqrt{1-4b^2z^2} + bc\sqrt{1-4a^2z^2}$ and $g_2 = 2az - y + y\sqrt{1-4a^2z^2}$. We now make the usual transformations to obtain the Morita approximation and note that the two square root singularities of Q correspond to delocalization into the two bulk phases (in the absence of a force), the zero ($z = z_3$) of g_1 corresponds to localization and the zero ($z = z_4$) of g_2 to the walk being pulled into the phase $x_2 > 0$ by the applied force. In each case we determine the value of L by applying the Morita condition that $\langle\sum_i \chi_i\rangle = n/2$. This gives

$$z_1 = \frac{1}{2\sqrt{a}} \qquad z_2 = \frac{1}{2\sqrt{b}} \qquad (61)$$

and

$$z_4 = \frac{y}{(1+y^2)\sqrt{a}}, \qquad (62)$$

together with a complicated expression for z_3. If we take $b > 1$ and $a < 1$ so that z_2 is the dominant singularity at zero force, the walk is delocalized into $x_2 < 0$. We then look for the value of y corresponding to $z_2 = z_4$. Making the substitutions $a = e^{-\epsilon/T}$, $b = e^{1/T}$ and $y = e^{f/T}$ gives the temperature dependence of the critical force, f, at fixed ϵ. If $\epsilon > 0$ the phase with $x_2 < 0$ will be preferred at zero force, and application of the force will pull the polymer from its preferred bulk phase into the less favourable bulk phase. The force-temperature diagram is given for several values of ϵ in Figure 3.

We can now ask how good the Morita approximation will be. In this case it is exact. It is easy to see that z_1 and z_2 are the exact values for the quenched case when the walk is in one or other of the two delocalized phases at zero force. This follows, for instance, by arguments similar to those of Martin et al. [19], adapted to the directed walk case. An argument similar to that given in Section 2 establishes that the Morita expression for z_4 is the exact value for the quenched case. Hence the Morita expression for the force is exact.

If $a, b < 1$ it is possible that z_3 will be dominant over z_1 and z_2 and the walk will be localized at the interface. In this case we can think of pulling the polymer out of the interface and into a bulk phase. To determine the critical value of the force we look for the value of y where $z_3 = z_4$ and make the substitutions $y = e^{f/T}$, $a = e^{-\epsilon/T}$ and $b = e^{-1/T}$. The temperature dependence of the critical force is shown in Figure 4 for several values of $\epsilon > 0$. There are several features worth noting. For all values of ϵ ($0 < \epsilon \leq 1$) the force increases with temperature at low temperature. For $0 < \epsilon < 1$ the force goes through a maximum and goes to zero at some finite temperature, while at $\epsilon = 1$ the force is not zero for any finite temperature. At fixed T the critical force increases as ϵ increases, since increasing ϵ corresponds to a worsening of the solvent into which the polymer is being pulled. We shall return to some of these issues in the next section.

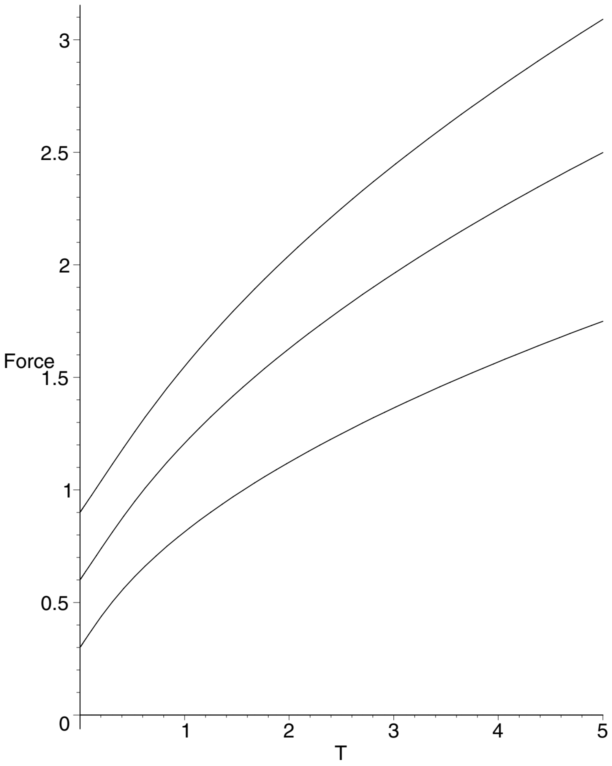

Fig. 3. The temperature dependence of the force required to pull a random copolymer from a preferred bulk phase to a less favourable bulk phase. The results are for a Dyck path model with $p = 1/2$. The upper curve is for $\epsilon = 0.8$, the middle curve for $\epsilon = 0.5$ and the lower curve is for $\epsilon = 0.2$.

In this case an argument similar to that given in Section 2 for adsorption establishes that the force calculated in the Morita approximation is an upper bound on the critical force for the quenched case.

4 Discussion

We have considered some directed walk models of a random copolymer subject to a force. Because of the difficulties of treating the quenched random case we have carried out the calculations in the Morita approximation which

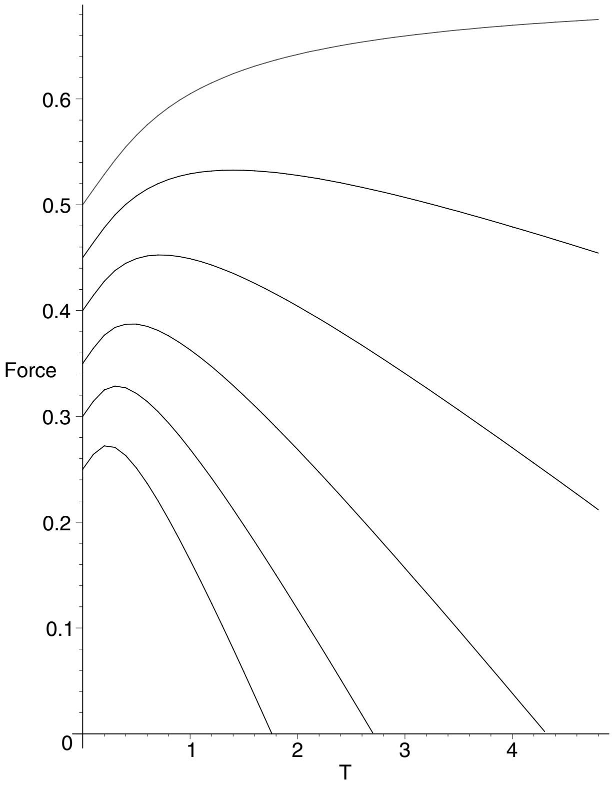

Fig. 4. The temperature dependence of the force required to pull a random copolymer localized at an interface into a bulk phase. The results are for a Dyck path model with $p = 1/2$. The top curve is for $\epsilon = 1$ and the others are for $\epsilon = 0.9$, 0.8, 0.7, 0.6 and 0.5.

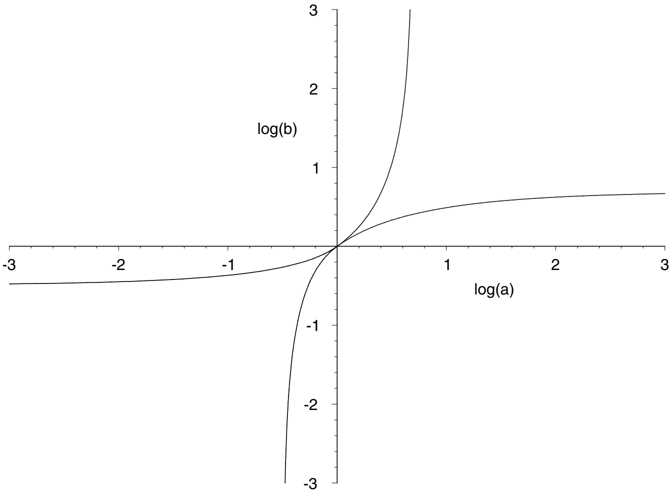

Fig. 5. The phase diagram for localization in the Morita approximation when $p = 1/2$. The polymer is delocalized into the β-phase throughout the second quadrant and into the α-phase throughout the fourth quadrant. There is a region of the third quadrant where the polymer has a positive density of vertices in the interface and is therefore localized.

can be considered as a partial annealing which ensures the correct frequency of occurence of the comonomers, although higher moments are not guaranteed. The approximation is known to give qualitatively correct results for the phase diagram of random copolymer localization without an applied force [7]. The phase diagram is shown in Figure 5.

The situations that we have considered are

1. a random copolymer adsorbed at an impenetrable surface (where only one comonomer interacts with the surface), where the force can cause desorption,
2. a random copolymer which is dissolved in one bulk phase and is pulled into a second (immiscible) bulk phase, and
3. a random copolymer localized at the interface between two immiscible bulk phases, which is pulled into one of the bulk phases.

In each case we considered a copolymer with two types of monomers (A and B) where the monomers are distributed independently with the probability that a monomer is A being p.

In the first case (random copolymer adsorption) we considered two models (related to Motzkin paths and to Dyck paths). We calculated the temperature dependence of the critical force required to desorb the copolymer. For $0 < p < 1$ the force has a maximum as the temperature increases (unlike the homopolymer case, where the force is monotone decreasing in temperature). This seems to be associated with the degenerate ground states of the models (at $T = 0$, $0 < p < 1$). If $p < 1$, at $T = 0$ all the A vertices of a Motzkin path will be in the surface but B vertices can be in or out of the surface. There are at least $2^{(1-p)n}$ such ground states so the intensive (reduced) entropy is at least $(1 - p)\log 2$. Hence the force-temperature curve will have a slope (at $T = 0$) at least as large as $(1-p)\log 2$. In Figure 1 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. For these models of random copolymer adsorption we showed that the critical force calculated in the Morita approximation is an upper bound on the force required for the quenched problem. Note that Figures 1 and 2 show that, within the Morita approximation, the force-temperature diagrams for Motzkin and Dyck path models are qualitatively similar. This could be understood by noticing that Dyck and Motzkin path models can be seen as two special cases of the same SOS model introduced some years ago to study the effect of disorder on two-dimensional wetting [20].

We also considered the situation where we have two immiscible solvents where the two types of comonomers have different energies of interaction with the two solvents. For this situation we modelled the polymer as a Dyck path. If the polymer is delocalized into one solvent (β, say) in the absence of a force and is pulled into the less favourable solvent (α, say), the required force is monotone increasing in the temperature. The critical force increases as the quality of the α solvent decreases. For this case we showed that the Morita approximation is in fact exact.

If $a, b < 1$ there is a region of the phase diagram (see Fig. 5) where the copolymer is localized at the interface (in the sense that the path crosses the interface a positive density of times). If we start at a point in this region and increase the temperature, we are following a ray in the third quadrant of the $(\log a, \log b)$-plane which ends at the origin (at infinite temperature). If the ray has unit slope (corresponding to $\epsilon = 1$ in our notation) the ray doesn't cross the phase boundary at any finite temperature, so the critical force is positive at every finite temperature. If the ray has any other slope then it crosses a phase boundary and if the slope is greater than unity (corresponding to $0 < \epsilon < 1$ in our notation) it crosses the phase boundary corresponding to delocalization into the α-phase. Hence, the critical force goes to zero at the temperature corresponding to the intersection point of the ray and this phase boundary. For this third case we showed that the Morita approximation gives a bound on the critical force for the quenched problem.

Finally we try to understand the positive slope of the force at low temperatures (in Fig. 4) by a qualitative argument. Recall that we are interested in the third quadrant where A vertices are repelled from the α-phase and B vertices are repelled from the β-phase. There is no energetic disadvantage for A (B) vertices to be in the interface $(x_2 = 0)$ or in the β-phase (α-phase). For any colouring sequence χ it is possible to construct a Dyck path such that no A (B) vertices will be in the α-phase (β-phase), by confining the vertices of the Dyck path to the three lines $x_2 = -1, 0, 1$. These will be ground state configurations, although other ground state configurations where the path is not confined to these three lines might also exist. For some colouring sequences the ground state will be unique while for others it will be degenerate. Consider a colouring χ which contains the sequence $\chi_1 = BABBBAB$, starting at an odd vertex. We write the vectors $(1, 1)$ as u and $(1, -1)$ as v. With the first vertex of this subwalk in $x_2 = 1$ the remainder of the subwalk can be $vuuvvu$ or $vuvuvu$. I.e. there are two possible subwalks with no A vertices in the α-phase and no B vertices in the β-phase. Since this colouring sequence (starting at an odd vertex) will occur on all except exponentially few sufficiently long walks at least $\epsilon_1 n$ times, for some $\epsilon_1 > 0$, there are at least $2^{\epsilon_1 n}$ possible ground states. Hence the entropy (per vertex) of the ground state is at least $\epsilon_1 \log 2$. (Of course, it is much larger than this since a similar argument can be made for other colouring subsequences.) This means that some entropy is lost when the walk is pulled off the surface so the force has positive slope at $T = 0$.

A problem closely related to the ones studied in this paper concerns the influence of disorder in the mechanical denaturation of DNA [21]. It would be interesting to see how the Morita approximation could be applied for that case.

This research was supported, in part, by NSERC of Canada.

References

1. C. Ortiz, G. Hadziioannou, Macromolecules **32**, 780 (1999)
2. J.E. Bemis, B.B. Akhremitchev, G.C. Walker, Langmuir **15**, 2799 (1999)
3. K. De'Bell, T. Lookman, Rev. Mod. Phys. **65**, 87 (1993)
4. C. Vanderzande, *Lattice Models of Polymers* (Cambridge University Press, Cambridge, 1998)
5. V. Privman, G. Forgacs, H.L. Frisch, Phys. Rev. B **37**, 9897 (1988)
6. S.G. Whittington, J. Phys. A **31**, 8797 (1998)
7. E. Orlandini, A. Rechnitzer, S.G. Whittington, J. Phys. A **35**, 7729 (2002)
8. E.J. Janse van Rensburg, J. Phys. A **36**, R11 (2003)
9. T. Garel, D.A. Huse, L. Leibler, H. Orland, Europhys. Lett. **8**, 9 (1989)
10. C. Monthus, Eur. Phys. J. B **13**, 111 (2000)
11. N. Madras, S.G. Whittington, J. Phys. A **36**, 923 (2003)
12. E. Bolthausen, F. den Hollander, Ann. Probab. **25**, 1334 (1997)
13. M. Biskup, F. den Hollander, Ann. Appl. Probab. **9**, 668 (1999)
14. E. Orlandini, M.C. Tesi, S.G. Whittington, J. Phys. A **37**, 1535 (2004)
15. R. Brout, Phys. Rev. **115**, 824 (1959)
16. T. Morita, J. Math. Phys. **5**, 1401 (1964)
17. E.W. James, C.E. Soteros, S.G. Whittington, J. Phys. A **36**, 11575 (2003)
18. R. Kühn, Z. Phys. B **100**, 231 (1996)
19. R. Martin, M.S. Causo, S.G. Whittington, J. Phys. A **33**, 7903 (2000)
20. G. Forgacs, J.M. Luck, Th.M. Nieuwenhuizen, H. Orland, J. Stat. Phys. **51**, 29 (1988)
21. D.K. Lubensky, D.R. Nelson, Phys. Rev. E **65**, 031917 (2002)