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Effect of stiffness on the pulling of an adsorbing polymer from a wall: an exact solution of a partially directed walk model

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Abstract

Recently the effect of stiffness, or semi-flexibility, on the adsorption and also the collapse phase transitions of isolated polymers has been explored via the exact solutions of partially directed walk models. Here we consider its effect on the stretching transition mediated by the application of a force to one end of the polymer when the other end is attached to an adsorbing wall.

PACS numbers: 05.50.+q, 05.70.fh, 61.41.+e

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

1. Introduction

The adsorption of polymers on a sticky wall, or walls, and more recently the pulling, or stretching, of a polymer away from a wall has been the subject of continued interest [1–10]. This has been in part due to the advent of experimental techniques that are able to micro-manipulate single polymers [11–13] and the connection to modelling DNA denaturation [14–20].

When a polymer in a dilute solution of ‘good’ solvent, so that it is in a swollen state [21], is attached to a wall at one end, the rest of the polymer drifts away due to entropic repulsion. It otherwise acts as if it were a free polymer. If the wall has an attractive contact potential so that it becomes ‘sticky’ to the monomers of the polymer, the polymer can be made to stay close to the wall by a sufficiently strong potential or at low enough temperatures. The second-order phase transition between these two states is the *adsorption* transition. The high-temperature state is *desorbed* while the low-temperature state is *adsorbed*. This pure adsorption transition has been well studied [1–3, 22, 23] exactly and numerically and demonstrated to be of second order.

The introduction of a pulling force away from the surface adds a third phase to this two-phase adsorption problem [5, 6, 8]. So, in addition to the desorbed and the adsorbed phases

a new phase, the *stretched* phase, where the polymer is stretched vertically away from the wall also appears in the phase diagram. In fact, the free desorbed phase only occurs when the vertical force is zero [5, 6]. At high temperatures any vertical force causes the polymer to be stretched vertically. At low temperatures, when at zero force the polymer is adsorbed, for sufficiently large forces away from the surface the adsorbed polymer can be made to go through a first-order transition to the *stretched* state.

The effect of stiffness, that is the consideration of semi-flexible polymers, has been examined in various contexts for both exactly solved lattice models [24–27] and canonical lattice models [28, 29]. In the exactly solved model of interacting partially directed self-avoiding walks (IPDSAW) the addition of stiffness was shown [26] to modify the associated phase transition of polymer collapse from second order (tricritical-like) to first order immediately upon application. Recently the effect of stiffness on the adsorption transition for partially directed walks was also examined via an exact solution [27]. For adsorption the effect of stiffness does not change the order of the transition though it does enhance the effect of the adsorbing potential, making it ‘easier’ to adsorb stiffened polymers.

Here we study the related exactly solvable model for polymer stretching, namely the partially directed self-avoiding walk (PDW) attached to a sticky wall with the addition of stiffness, and being stretched both horizontally and vertically. Hence we consider the effect of stiffness and horizontal elongation on the stretching problem described above. We also compare the effect of horizontal elongation to the effect of stiffness. The work here builds on various works in the literature and being currently undertaken [1, 27, 30–32]. The results here give a four-dimensional phase diagram in surface binding potential, stiffness, horizontal elongation force and vertical force.

2. Model

Consider a square lattice and a self-avoiding walk of L steps such that it has one end fixed at the origin of the lattice. If (x_i, y_i) are the coordinates of the sites of the lattice occupied by walk for $i = 0, 1, \dots, L$, then $(x_0, y_0) = (0, 0)$. Now restrict the configurations considered to self-avoiding walks such that starting at the origin only steps in $(1, 0)$, $(0, 1)$ and $(0, -1)$ are permitted: such a walk is known as a partially directed self-avoiding walk (PDW). Immediately we note that $x_i \geq 0$. We introduce a surface at $y = 0$ by considering only those walks with every site of the walk lying on the upper half-plane with $y_i \geq 0$ for all i . For convenience, we consider walks whose last step is horizontal. An example configuration, along with the associated variables of our model, is illustrated in figure 1. We note that our walks may end at any height above the surface.

We add an energy for steps of the walk that lie on the surface (wall) to give the adsorbing polymer model: see figure 1. An energy $-J$ is added for each such *visit*. We define a Boltzmann weight $\kappa = e^{\beta J}$ associated with these visits, where $\beta = 1/k_B T$, k_B is Boltzmann’s constant and T is the absolute temperature. We also add an energy $-\Delta$ to each site (*stiffness* site) between consecutive horizontal steps of the walk: see figure 1. For $\Delta > 0$ consecutive horizontal steps are favoured and so this is the positive stiffness, or the semi-flexible, regime. For $\Delta < 0$ consecutive horizontal steps are discouraged, so this is a negative stiffness regime where bends are encouraged.

We have chosen to weight horizontal straight segments in our stretching model to mimic the collapse and adsorption models previously analysed [26, 27]. On the other hand, one may model stiffness, perhaps more naturally, by rather introducing a weighting for bends of the walk. In fact, our model is equivalent to one where bends are weighted and a rescaled horizontal force is applied [27]. As can be seen below, the application of any horizontal force

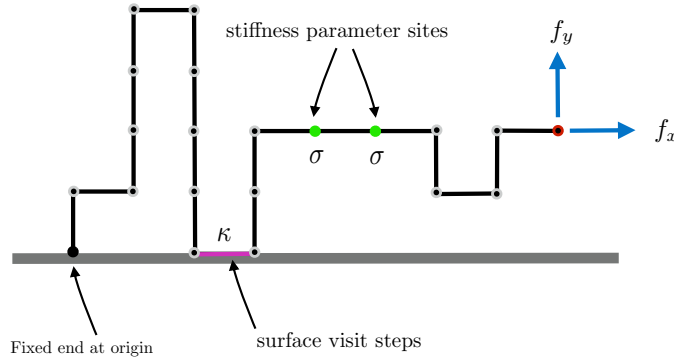


Figure 1. An example of a partially directed walk of length $L = 20$, width $N = 8$ and whose rightmost horizontal step is at height $r = 2$ above a surface, with the parameters κ associated with ‘visits’ of walk steps with the surface and the stiffness parameter σ associated with the sites (highlighted) between two consecutive horizontal steps. A force f_x is applied horizontally to the non-fixed end giving rise to a Boltzmann factor p^N , while a force f_y is applied vertically to the non-fixed end giving rise to a Boltzmann factor h^r . The Boltzmann weight of the configuration shown is $\kappa \sigma^2 h^2 p^8$.

does not change the type of phase transition. We note however that while adding stiffness to vertical segments will not change the nature of the phase transitions which is our primary focus here, it will change the shape of critical temperature plots: in particular enhancing vertical stiffness will enhance the relative effect of the vertical force and make adsorption more difficult.

If ℓ is the number of such *stiffness* sites in a particular PDW, then such a configuration is associated with an additional Boltzmann factor σ^ℓ where $\sigma = e^{\beta \Delta}$. A force f_x is applied horizontally to the non-fixed end giving rise to a Boltzmann weight factor per unit horizontal extension of the walk $p = e^{\beta f_x}$. A force f_y is applied vertically to the non-fixed end giving rise to a Boltzmann weight factor per unit vertical extension of the walk $h = e^{\beta f_y}$.

The polymer partition function $P_L(\kappa, \sigma, p, h)$ for configurations of our model is

$$P_L(\kappa, \sigma, p, h) = \sum_{\text{PDW } \psi_L \text{ of length } L} \kappa^{m(\psi_L)} \sigma^{\ell(\psi_L)} p^{N(\psi_L)} h^{r(\psi_L)}, \quad (2.1)$$

where $m(\psi_L)$ is the number of steps of the walk configuration ψ_L on the surface, $\ell(\psi_L)$ is the number of stiffness sites, $N(\psi_L)$ is the horizontal width of the walk and $r(\psi_L)$ is the height of the end of the walk. The coordinates of the site being pulled are (N, r) and so the end-to-end displacement has the components N and r in the x and y directions, respectively. The generating function $F(z, \kappa, \sigma, p, h)$ we shall calculate is

$$F(z, \kappa, \sigma, p, h) = \sum_{L=1}^{\infty} P_L(\kappa, \sigma, p, h) z^L. \quad (2.2)$$

The singularity structure of the generating function as a function of z determines the free energy. The reduced free energy is defined as

$$f(\kappa, \sigma, p, h) = - \lim_{L \rightarrow \infty} \frac{1}{L} \log(P_L(\kappa, \sigma, p, h)) \quad (2.3)$$

and is given by

$$f(\kappa, \sigma, p, h) = \log z_s(\kappa, \sigma, p, h), \quad (2.4)$$

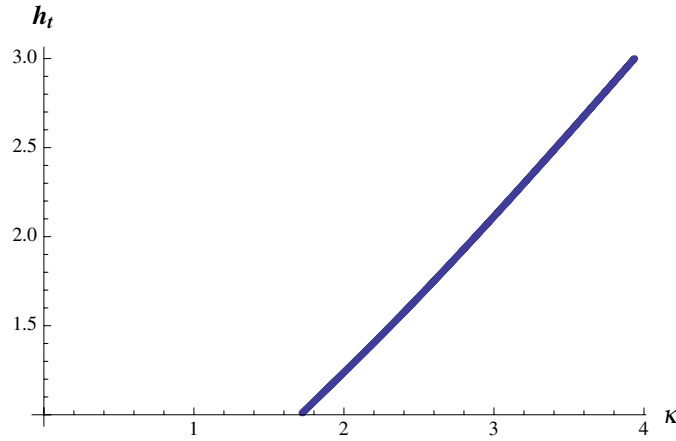


Figure 2. A plot of the Boltzmann weight associated with the critical vertical force $h_t(\kappa)$ against κ for fully flexible polymers ($\sigma = 1$) and no horizontal force ($f_x = 0$). As $\kappa \rightarrow (1 + 1/\sqrt{2})^+$ we have that $h_t(\kappa) \rightarrow 0$ since without a force the adsorption transition takes place at $\kappa = \kappa_A = 1 + 1/\sqrt{2}$ for the PDW.

where $z_s(\kappa, \sigma, p, h)$ is the closest singularity (on the positive real axis) of the generating function $F(z, \kappa, \sigma, p, h)$ in the variable z to the origin.

3. Characterization of the phases

From [5, 27, 30] we do not expect that the introduction of stiffness and horizontal elongation will introduce new phases into the adsorption/stretching problems. As mentioned in the introduction we expect three phases: a free *desorbed* phase that occurs when $f_y = 0$ ($h = 1$) at high temperatures (small κ); an *adsorbed* phase that occurs when κ is large and h is small enough; and a *stretched* phase that occurs when a sufficient positive vertical force is applied.

Without stiffness ($\sigma = 1$) and horizontal elongation ($p = 1$) there is a single adsorption transition at $\kappa = \kappa_t$ when $h = 1$ [1]. This occurs at $\kappa_t = 1 + 1/\sqrt{2}$ for the PDW. When $h > 1$, there is a transition between the stretched and adsorbed phases at $h = h_t(\kappa)$, or alternatively $\kappa = \kappa_t(h)$. Figure 2 shows a plot of the critical Boltzmann weight h_t associated with the force f_y against the Boltzmann weight controlling the stickiness of the wall κ for our partially directed walk model without stiffness ($\sigma = 1$) or horizontal elongation ($p = 1$). We have that $h_t(\kappa) > 0$ only when $\kappa > 1 + 1/\sqrt{2}$ and is an increasing function of κ .

For the sake of comparison, in terms of the physical variables, temperature and vertical force, the variation of the critical force with temperature is given in figure 3.

Two key thermodynamic quantities, \mathcal{M} and \mathcal{R} , can be defined that describe the phases of the system. Firstly, \mathcal{M} is the average number of steps of the walk located on the surface per step of the walk

$$\mathcal{M}(\kappa, \sigma, p, h) = \lim_{L \rightarrow \infty} \left\langle \frac{m}{L} \right\rangle = \lim_{L \rightarrow \infty} \frac{\sum_{\psi_L} m(\psi_L) \kappa^{m(\psi_L)} \sigma^{\ell(\psi_L)} p^{N(\psi_L)} h^{r(\psi_L)}}{L P_L(\kappa, \sigma, p, h)}, \quad (3.1)$$

which implies

$$\mathcal{M}(\kappa, \sigma, p, h) = \lim_{L \rightarrow \infty} \frac{\kappa}{L} \frac{d \log(P_L(\kappa, \sigma))}{d \kappa} = -\kappa \frac{d \log z_s(\kappa, \sigma, p, h)}{d \kappa}. \quad (3.2)$$

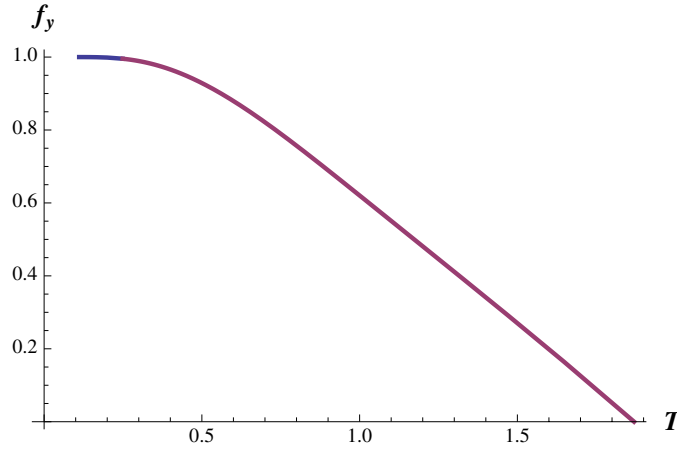


Figure 3. A plot of the critical force against temperature for fully flexible polymers with $\Delta = 0$. We have normalized $J/k_B = 1$ and chosen $f_x = 0$.

Hence the variation of z_s with κ is directly related to the average occupation of the surface by the walk. Secondly, \mathcal{R} is defined as

$$\mathcal{R}(\kappa, \sigma, p, h) = \lim_{L \rightarrow \infty} \left\langle \frac{r}{L} \right\rangle = \frac{\sum_{\psi_L} r(\psi_L) \kappa^{m(\psi_L)} \sigma^{\ell(\psi_L)} p^{N(\psi_L)} h^{r(\psi_L)}}{L P_L(\kappa, \sigma, p, h)}, \quad (3.3)$$

which implies

$$\mathcal{R}(\kappa, \sigma, p, h) = \lim_{L \rightarrow \infty} \frac{h}{L} \frac{d \log(P_L(\kappa, \sigma, p, h))}{dh} = -h \frac{d \log z_s(\kappa, \sigma, p, h)}{dh}, \quad (3.4)$$

where r is the height of the end of the walk from the surface. Hence, the variation of z_s with h is directly related to the average height of the endpoint from the surface by the wall.

In the *desorbed* phase we have $\mathcal{M} = \mathcal{R} = 0$, in the *adsorbed* phase $\mathcal{M} > 0$ while $\mathcal{R} = 0$, and in the *stretched* phase $\mathcal{R} > 0$ while $\mathcal{M} = 0$. Hence one can use \mathcal{R} and \mathcal{M} as order parameters for the phase transitions in the system.

We expect the desorbed and adsorbed phases along with the adsorption transition to occur when there is no vertical force $h = 1$ for all σ and p . So let us define the position of adsorption transition as occurring at $\kappa_A(\sigma, p)$ with $\kappa_A(1, 1) = 1 + 1/\sqrt{2}$. Once $h > 1$ we expect the two phases stretched and adsorbed with a transition occurring at $\kappa_t(\sigma, p, h)$. We expect $\lim_{h \rightarrow 0} \kappa_t(\sigma, p, h) = \kappa_A(\sigma, p)$ and so use $\kappa_t(\sigma, p, 1) = \kappa_A(\sigma, p)$.

A more refined description of the phases and the adsorption critical point can be obtained by consideration of various exponents. Let us define the following exponents: for $L \rightarrow \infty$ we expect

$$P_L \sim A e^{f(\kappa, \sigma, p, h)L} L^{\gamma_{11}-1}, \quad (3.5)$$

alternately via the generating function $F(z) \sim B(z_s - z)^{-\gamma_{11}}$ as $z \rightarrow z_s^-$,

$$\langle m \rangle \sim C L^{\phi_s}, \quad (3.6)$$

$$\langle N \rangle \sim D L^{\nu_{\parallel}} \quad (3.7)$$

and

$$\langle r \rangle \sim E L^{\nu_{\perp}}. \quad (3.8)$$

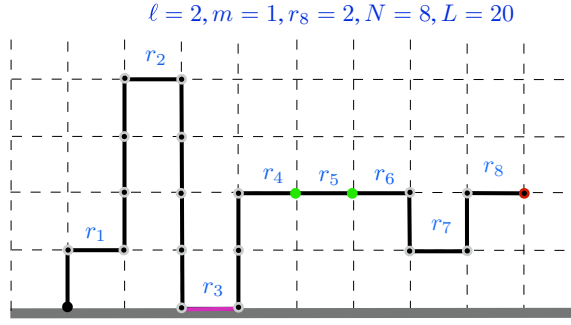


Figure 4. An example of a partially directed walk given by the values of the defining variables r_i , $i = 1, \dots, 8$. These give the heights of the horizontal steps above the surface: here we have $r_1 = 1, r_2 = 4, r_3 = 0, r_4 = r_5 = r_6 = 2, r_7 = 1, r_8 = 2$. The generating function weight of this configuration is $x^8 y^{12} \kappa \sigma^2 h^2 p^8$.

At the adsorption critical point the exponent ϕ_s becomes the crossover exponent $\phi = 1/2$ for the transition [2]. From the solution of the model when $\sigma = p = 1$ [1, 30] the desorbed phase can be seen to exhibit $\gamma_{11} = 1/2, \phi_s = 0, v_{\parallel} = 1, v_{\perp} = 1/2$ while the adsorbed phase has $\gamma_{11} = 1, \phi_s = 1, v_{\parallel} = 1, v_{\perp} = 0$. At the adsorption transition $\gamma_{11} = 1, \phi_s = 1/2, v_{\parallel} = 1, v_{\perp} = 1/2$. From work on similar models [5] the stretched phase has $\gamma_{11} = 1, \phi_s = 0, v_{\parallel} = 1, v_{\perp} = 1$.

4. Solution setup

To solve for our generating function we define the configurations of our PDW through a set of variables r_i describing the height of each horizontal step of our walk in column i of our lattice: here column i is bounded by vertices of the lattice with x -coordinates $i - 1$ and i . See figure 4. The energy of a configuration is

$$-\beta E(r_0; r_1, \dots, r_N) = \beta J \sum_{i=1}^N \delta_{r_i, 0} + \beta \Delta \sum_{j=1}^N \delta_{r_{j-1}, r_j} + \beta f_x \sum_{j=1}^N 1 + \beta f_y r_N, \quad (4.1)$$

where we define $r_0 = 0$ for convenience.

Now let us define a restricted energy

$$-\beta \bar{E}(r_0; r_1, \dots, r_N) = \beta J \sum_{i=1}^N \delta_{r_i, 0} + \beta \Delta \sum_{j=1}^N \delta_{r_{j-1}, r_j}. \quad (4.2)$$

For calculational convenience we define the partial generating functions for paths of fixed width N with ends fixed at heights $r_0 = 0$ and $r_N \geq 0$. Defining a fugacity y for vertical steps we define the ‘finite-width’ generalized partition function as

$$Z_1(r_1) = y^{r_1} \exp(-\beta E(0; r_1)) \quad (4.3)$$

and

$$Z_N(r_N) = \sum_{r_1, \dots, r_{N-1} \geq 0} y^{L-N} \exp(-\beta E(0; r_1, \dots, r_N)), \quad N = 2, 3, \dots \quad (4.4)$$

Let us also define

$$\bar{Z}_1(r_1) = y^{r_1} \exp(-\beta \bar{E}(0; r_1)) \quad (4.5)$$

and

$$\bar{Z}_N(r_N) = \sum_{r_1, \dots, r_{N-1} \geq 0} y^{L-N} \exp(-\beta \bar{E}(0; r_1, \dots, r_N)), \quad N = 2, 3, \dots \quad (4.6)$$

We immediately have that

$$Z_N(r) = p^N h^r \bar{Z}(r). \quad (4.7)$$

Let $x = p\hat{x}$. We define the generating function for walks that end at a fixed height r as

$$G_r(x, y, \kappa, \sigma, h) = \sum_{N=1}^{\infty} Z_N(r) \hat{x}^N = h^r \sum_{N=1}^{\infty} \bar{Z}_N(r) x^N. \quad (4.8)$$

Letting

$$G_r = h^r g_r \quad (4.9)$$

the generating function we need is

$$G(x, y, \kappa, \sigma, h) = \sum_{r=0}^{\infty} G_r(x, y, \kappa, \sigma, h) = \sum_{r=0}^{\infty} h^r g_r(x, y, \kappa, \sigma). \quad (4.10)$$

We are interested in finding the generating function

$$F(z, \kappa, \sigma, p, h) = G(pz, z, \kappa, \sigma, h) = \sum_{r=0}^{\infty} h^r g_r(pz, z, \kappa, \sigma). \quad (4.11)$$

5. Exact solution of the generating functions

5.1. Intermediate results

Importantly the generating function $g_r(x, y, \kappa, \sigma)$ was calculated in [27] as

$$g_r(x, y, \kappa, \sigma) = A \lambda_Z^{r-1} \quad \text{for } r \geq 1 \quad (5.1)$$

and

$$g_0(x, y, \kappa, \sigma) = wu + wu \frac{A}{1 - y\lambda_Z}. \quad (5.2)$$

Here $\lambda_Z \equiv \lambda_Z(x, y, \sigma)$ while $A \equiv A(x, y, \kappa, \sigma)$.

Defining

$$u = \frac{x}{1 - x(\sigma - 1)}, \quad (5.3)$$

$$v = \frac{\kappa(1 - x(\sigma - 1))}{1 - x\kappa(\sigma - 1)}, \quad (5.4)$$

$$w = \frac{v}{1 - vu}, \quad (5.5)$$

$$\rho(u, y) = \left(y + \frac{1}{y}\right) + u \left(y - \frac{1}{y}\right) = \frac{1}{y} [1 + y^2 - u(1 - y^2)] \quad (5.6)$$

and

$$\begin{aligned} \lambda_Z &= \hat{\lambda}(u, y) = \frac{1}{2}(\rho - \sqrt{\rho^2 - 4}) \\ &= \frac{1}{2y} [1 + y^2 - u(1 - y^2) - \sqrt{[(1 + u^2)(1 - y^2) - 2u(1 + y^2)](1 - y^2)}]. \end{aligned} \quad (5.7)$$

Note that

$$\hat{\lambda}^2 - \rho(u, y)\hat{\lambda} + 1 = 0; \quad (5.8)$$

we have

$$A = \frac{uy(1+wu)(1-y\hat{\lambda})}{1-y\hat{\lambda}-u[1+wuy^2]}. \quad (5.9)$$

Now using the same underlying algebra as in [27] we have

$$g_0(x, y, \kappa, \sigma) = \frac{\kappa u(1-y^2)}{1-uv(1-y^2)-y\hat{\lambda}(u, y)}. \quad (5.10)$$

Hence the generating function we require is

$$G(x, y, \kappa, \sigma, h) = g_0 + \sum_{r=1}^{\infty} h^r g_r = g_0 + A \sum_{r=1}^{\infty} h^r \hat{\lambda}^{r-1} = g_0 + \frac{Ah}{1-h\hat{\lambda}} \quad (5.11)$$

giving

$$G(x, y, \kappa, \sigma, h) = \frac{u(1-y^2)[(1-v)\hat{\lambda}(u, y) + v]}{[1-uv(1-y^2)-y\hat{\lambda}(u, y)](1-h\hat{\lambda}(u, y))}. \quad (5.12)$$

5.2. The full solution

This gives the main result of this paper as the full generating function in terms of the original variables as

$$F(z, \kappa, \sigma, p, h) = \frac{pz(1-y^2)[(1-\kappa)\lambda + \kappa(1-pz(\sigma-1))]}{(1-pz(\sigma-1))[(1-z\lambda)(1-\kappa pz(\sigma-1)) - \kappa pz(1-z^2)](1-h\lambda)} \quad (5.13)$$

with

$$\lambda \equiv \lambda(z, \sigma, p) = \frac{1}{2z} \left[1 + z^2 - u(1-z^2) - \sqrt{[(1-z^2)(1+u^2) - 2u(1+z^2)](1-z^2)} \right], \quad (5.14)$$

$$u(z, \sigma, p) = \frac{pz}{1-pz(\sigma-1)}. \quad (5.15)$$

6. Analysis of the phase diagram

As we have argued that the behaviour is essentially dependent on whether $h = 1$ or not, we consider these cases separately.

6.1. Analysis for $h = 1$

We expect a single adsorption transition between desorbed polymers at small κ and adsorbed polymers at large κ . This analysis generalizes the results in [27] to the case $p \neq 1$ and similarly the results in [31] to the case $\sigma \neq 1$. The algebraic singularity arising from λ occurs when the discriminant is zero at $z = z_d$: namely, at

$$([1 - p(\sigma-1)z_d]^2 + p^2 z_d^2)(1 - z_d^2) - 2pz_d(1 + z_d^2)(1 - p(\sigma-1)z_d) = 0. \quad (6.1)$$

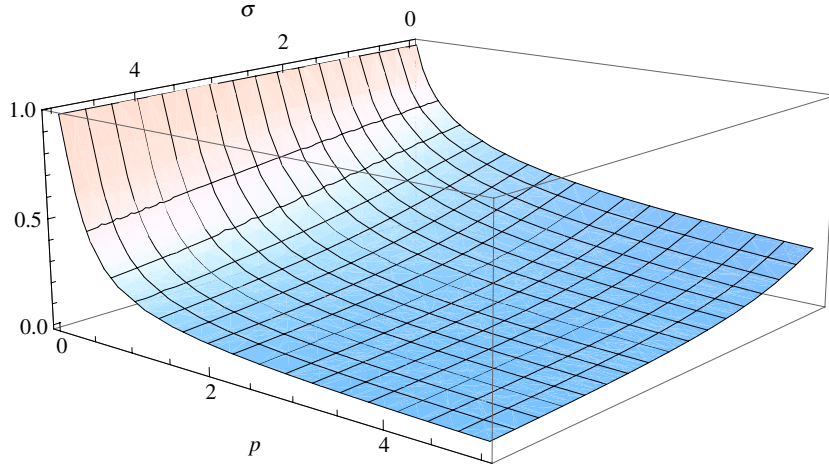


Figure 5. A plot of the desorbed singularity value $z_d(\sigma, p)$ against σ and p .

This can be factorized to show that the *desorbed* singularity z_d obeys

$$1 - (p\sigma + 1)z_d + p(\sigma - 2)z_d^2 = 0. \quad (6.2)$$

This gives

$$z_d(\sigma, p) = \frac{1 + p\sigma - \sqrt{1 + 8p - 2p\sigma + p^2\sigma^2}}{2p(\sigma - 2)}. \quad (6.3)$$

One can readily discover that the solution $z_d(\sigma, p)$ is a monotonically decreasing function of σ at fixed p and a monotonically decreasing function of p at fixed σ : see figure 5. Note that $\lambda(z_d(\sigma, p), \sigma, p) = 1$.

The other singularity, which gives rise to a simple pole in the generating function away from the transition, occurs when

$$(1 - z\lambda)(1 - z\kappa p(\sigma - 1)) - \kappa pz(1 - z^2) = 0, \quad (6.4)$$

that is,

$$\kappa = \frac{(1 - z\lambda)}{pz(1 - z^2) + (\sigma - 1)pz(1 - z\lambda)}, \quad (6.5)$$

giving $z = z_a(\kappa, \sigma, p)$ (the *adsorbed* singularity) implicitly.

The two singularities coincide when $z_a = z_d$ with $\lambda = 1$, that is,

$$\begin{aligned} \kappa_t(\sigma, p) &= \frac{1}{p(\sigma z_d + z_d^2)} \\ &= \frac{4p^2(\sigma - 2)^2}{[1 + p\sigma - \sqrt{1 + p(8 + \sigma(p\sigma - 2))}][1 - p(1 + 2p(\sigma - 2))\sigma - \sqrt{1 + p(8 + \sigma(p\sigma - 2))}]}. \end{aligned} \quad (6.6)$$

A surface plot of $\kappa_t(\sigma, p)$ can be found in figure 6. The function $\kappa_t(\sigma, p)$ is a monotonically decreasing function of σ at fixed p and a monotonically decreasing function of p at fixed σ (see figure 7). Hence the sticky potential needed to adsorb the polymer on the wall decreases with increasing stiffness and with increasing elongation (horizontal) force: it is easier to adsorb stiff or elongated polymers. As an aside, it should be stressed that $\kappa_t(\sigma, p)$ is an analytic

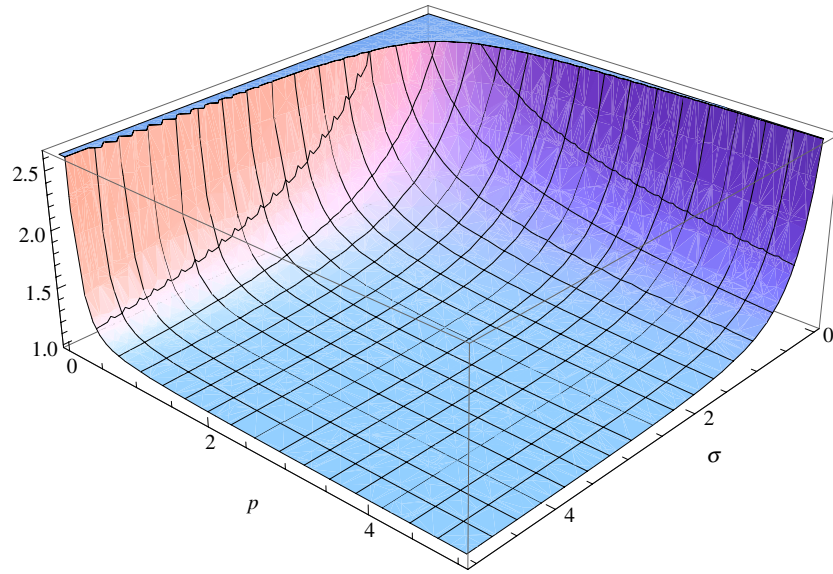


Figure 6. A surface plot of $\kappa_t(\sigma, p)$ against σ and p .

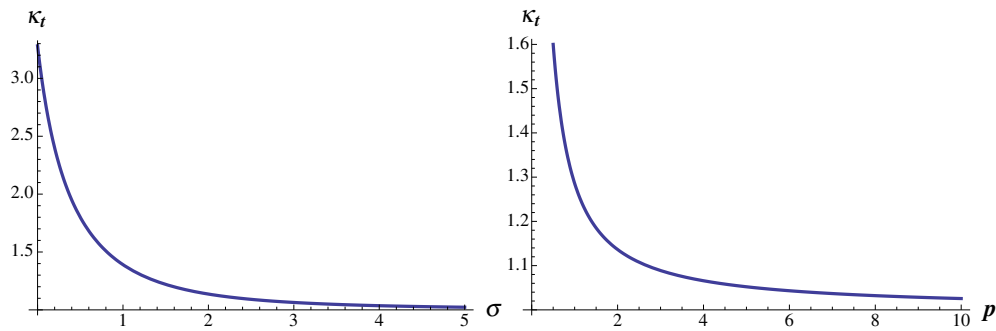


Figure 7. A plot of $\kappa_t(\sigma, p)$ against σ for $p = 2.0$ (left) and a plot of $\kappa_t(\sigma, p)$ against p for $\sigma = 2.0$ (right).

function of σ for positive real σ including $\sigma = 2$. In figure 8 we also show two plots in terms of the physical variables temperature T and horizontal force f_x of the effect of an horizontal force on the critical temperature (we have normalized $J/K_b = 1$). The effect of horizontal stiffness is the increase in the critical temperature, as one might expect.

The adsorbed singularity only occurs when $\kappa \geq \kappa_t$ and for $\kappa > \kappa_t$ it is the closest singularity to the origin. In figure 9 we have $z_s(\kappa, 1.5, 1.5)$ plotted against κ : the smooth transition at $\kappa \approx 1.2921$ is visible.

Regardless of σ and p it is crucial to realize that λ has the expansion

$$\lambda = 1 - c\sqrt{(z_d - z)} + O((z_d - z)) \quad (6.7)$$

for $z \rightarrow z_d^-$. By expanding the denominator factor (6.4) about $z = z_d$ and $\kappa = \kappa_t$ and assuming $z < z_d$ and $\kappa > \kappa_t$ one can deduce that

$$z_a = z_d - c_2(\kappa - \kappa_t)^2 + O((\kappa - \kappa_t)^3). \quad (6.8)$$

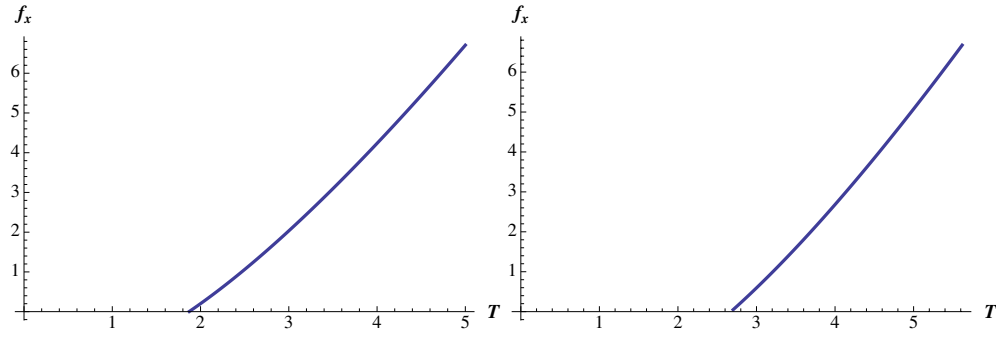


Figure 8. A plot of the critical temperature T_t against a horizontal force (vertical axis) for fully flexible polymers with $\Delta = 0$ (left) and for semi-flexible polymers with $\Delta = J$ (right). We have normalized $J/k_B = 1$.

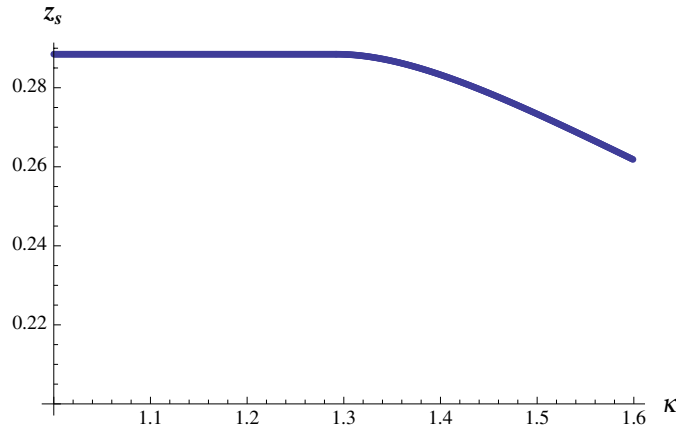


Figure 9. A plot of z_s against κ for $\sigma = p = 1.5$. At $\sigma = p = 1.5$ we have the desorbed value $z_d(1.5, 1.5) = 0.288487\dots$. The value of κ at the transition is $\kappa_t(1.5, 1.5) = 1.2921\dots$.

Since $z_s = z_d$ for $\kappa < \kappa_t$ this implies that the specific heat exponent $\alpha = 2$, that is, the adsorption transition is of second order. It also implies that \mathcal{M} vanishes linearly with $(\kappa - \kappa_t)$.

6.2. Analysis of full model

We now expect three phases as described in the previous sections. This generalizes the work in [32] to the case $p \neq 1$. When $h \neq 1$, a third potential singularity $z_h(\sigma, p, h)$ arises in the generating function at

$$\lambda(z_h, \sigma, p) = 1/h, \quad (6.9)$$

that is, using the fact that $\lambda + 1/\lambda = \rho$, the solution of the cubic is

$$(\sigma - 2)hpz^3 - (p(1 + h^2)(\sigma - 1) + h)z^2 + (1 + h^2 + hp\sigma)z - h = 0. \quad (6.10)$$

One needs to be careful in taking the smallest positive solution of the equation since the coefficient of the cubic term changes sign as σ moves through 2. For $\sigma = 2$ one has a

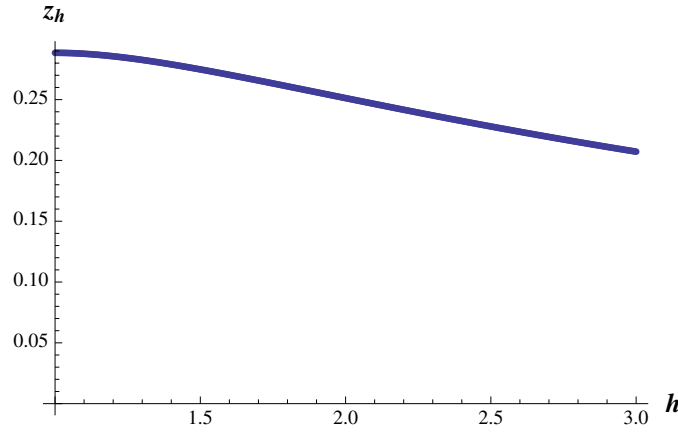


Figure 10. A plot of the stretched singularity value $z_h(\sigma, p, h)$ against h for $\sigma = p = 1.5$. The limit $\lim_{h \rightarrow 0} z_h(1.5, 1.5, h) = 0.288\,487\dots = z_d(1.5, 1.5)$.

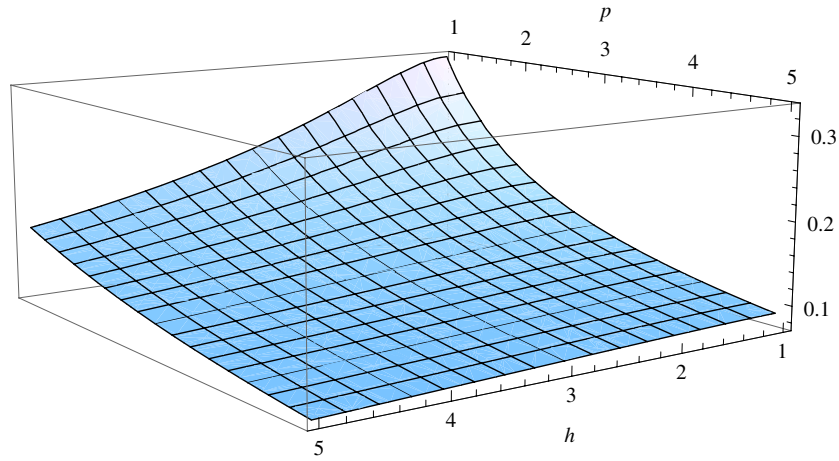


Figure 11. A surface plot of the stretched singularity value $z_h(2.0, p, h)$ against p and h .

quadratic and so a simple expression for z_h as

$$z_h(2, p, h) = \frac{1 + h^2 + 2hp - \sqrt{1 - 2h^2 + h^4 + 4h^2 p^2}}{2(h + p + h^2 p)}. \quad (6.11)$$

The generating function has a simple pole at z_h . A plot of $z_h(1.5, 1.5, h)$ can be found in figure 10, while a surface plot of $z_h(2.0, p, h)$ can be found in figure 11. As we know that $\lambda = 1$ when the discriminant of equation (5.14) vanishes and also that λ is an increasing function of z , we deduce that for $h > 1$ we have

$$z_h < z_d \quad (6.12)$$

and hence a new phase structure emerges. Note that since z_h is a non-constant function of h , we have $\mathcal{R} \neq 0$ via equation (3.4).

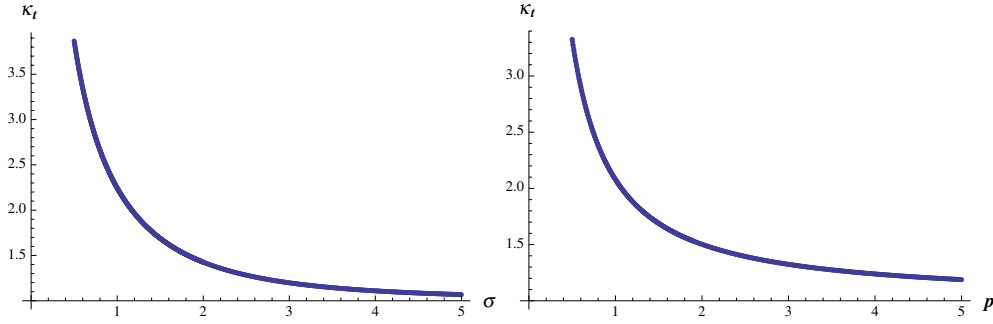


Figure 12. A plot of $\kappa_t(\sigma, p, h)$ against σ for $h = 2$ when $p = 1.5$ (left) and a plot of $\kappa_t(\sigma, p, h)$ against p for $h = 2$ when $\sigma = 1.5$.

The singularity at z_h is associated with a polymer that is stretched away from the surface rather than simply freely unbound, as happens at z_d . Since for any σ and p $z_h < z_d$ when $h > 1$, the desorbed singularity plays no role in the analysis of the $h > 1$ problem: the desorbed phase does not appear when a vertical force is applied.

On the other hand, the *adsorbed* singularity z_a which is independent of h is still dominant (that is, when z_a is the closest singularity to the origin) for large enough κ . From our analysis of the $h = 1$ case we have the location of the adsorbed singularity $z = z_a(\kappa, \sigma, p)$ via

$$\kappa = \frac{(1 - z\lambda)}{pz(1 - z^2) + (\sigma - 1)pz(1 - z\lambda)}. \quad (6.13)$$

In the adsorbed phase $\mathcal{R} = 0$ since z_a is independent of h .

The *stretched* singularity, z_h , coincides with the *adsorbed* one, z_a , when $z_a = z_h$, that is,

$$\kappa_t(\sigma, p, h) = \frac{(1 - z_h/h)}{pz_h(1 - z_h^2) + (\sigma - 1)pz_h(1 - z_h/h)}. \quad (6.14)$$

As with $h = 1$, for $h > 1$ the function $\kappa_t(\sigma, p, h)$ is a monotonically decreasing function of σ at fixed p and a monotonically decreasing function of p at fixed σ : plots of $\kappa_t(\sigma, p, h)$ can be found in figure 12.

At fixed σ and p the position of the adsorbed singularity $z_a(\kappa, \sigma, p)$ does not change with h , though it decreases with increasing κ . Since z_h decreases with h , the value of κ which gives $z_a = z_h$ must increase with h . That is, we have argued that $\kappa_t(\sigma, p, h)$ is an *increasing* function of h at fixed σ and p . One can also consider the value of h at the stretching transition for fixed large κ . Equation (6.14) can be inverted to find that transition value of h , which we denote as $h_t(\kappa, \sigma, p)$. A plot of $h_t(\kappa, 1.5, 1.5)$ is given in figure 13. Clearly, since κ_t increases with h , this means that h_t increases with κ .

In figure 14 there is a surface plot of $\kappa_t(2.0, p, h)$ against p and h . Note that κ_t increases with h and decreases with p and so if a polymer is pulled at a fixed small angle, it can be adsorbed even though it is being pulled off the surface: this result generalizes the intriguing observation¹ made by Osborn and Prellberg [31] for $\sigma = 1$.

Recalling $\kappa_A(\sigma, p) = \kappa_t(\sigma, p, 1)$ we have that the adsorbed singularity only occurs when $\kappa \geq \kappa_A$. However, it is only for $\kappa > \kappa_t > \kappa_A$ that it is the closest singularity to the origin. In figure 15 $z_s(\kappa, 1.5, 1.5, 2)$ is plotted against κ . The transition, which is marked by an abrupt

¹ We also direct the interested reader to Osborn and Prellberg [31] for the description of this in terms of the physical variables temperature, horizontal and vertical forces.

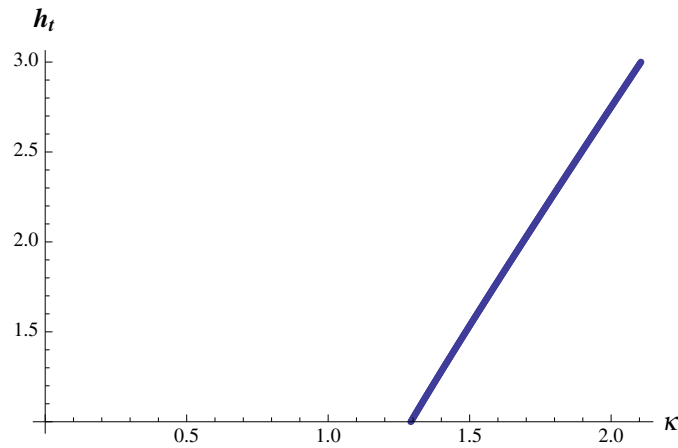


Figure 13. A plot of $h_t(\kappa, p, h)$ against κ for $\sigma = p = 1.5$.

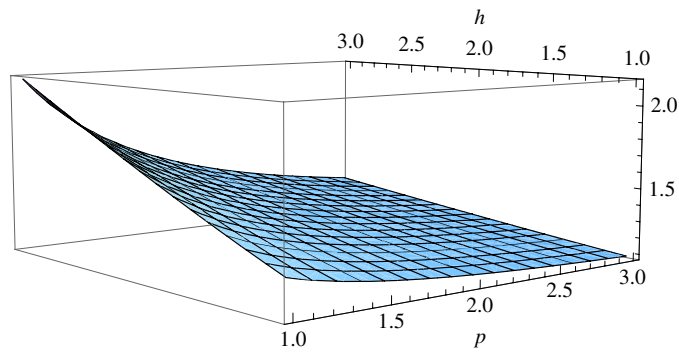


Figure 14. A surface plot of $\kappa_t(2.0, p, h)$ against p and h .

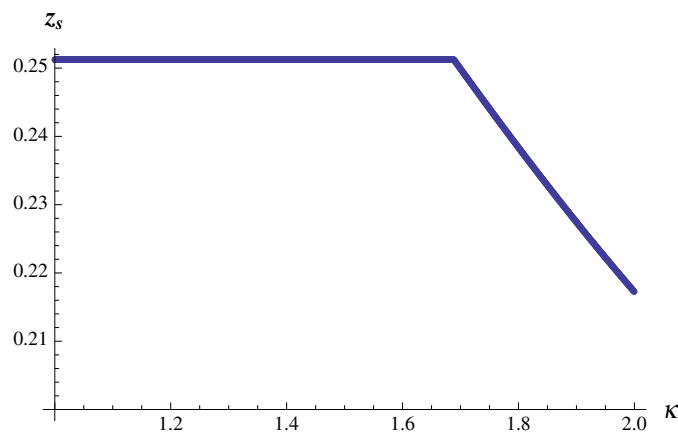


Figure 15. A plot of z_s against κ for $h = 2$ with $\sigma = p = 1.5$. The stretched value $z_h = 0.251\,233\dots$. There is a sharp change in the slope of the curve at $\kappa_t = 1.688\,59\dots$.

change in the slope of z_s , occurs at $\kappa_t = 1.688\,59\dots$. This abrupt change of slope is a sign of a first-order transition. To see this more generally we see that $\lambda(z, \sigma, p)$ is a monotonically increasing analytic function of z for $0 \leq z \leq z_d(\sigma, p)$. Since $z_h < z_d$ clearly

$$\lambda = 1/h + c_1(z_h - z) + O((z_h - z)^2) \quad (6.15)$$

for z near z_h . Analysing equation (6.13) near κ_t , this implies that for $\kappa \approx \kappa_t$

$$z_a = z_h - c_2(\kappa - \kappa_d) + O((\kappa - \kappa_d)^2). \quad (6.16)$$

Since $z_s = z_h$ for $\kappa < \kappa_t$ when $h > 1$, this implies that the specific heat exponent $\alpha = 1$, that is, the adsorption transition is of first order regardless of σ and p .

The other exponents γ_{11} , v_{\parallel} , v_{\perp} and ϕ_s for each of the phases do not depend on σ and p other than via the location of those phases.

7. Conclusions

We have considered a partially directed walk model of a semi-flexible polymer, attached at one end to a sticky surface, that is being stretched both horizontally and vertically. The main results of our work stem from the exact solution of the model, the nature of the associated phase transitions and the comparisons with earlier works [26, 27]. Additionally, our physically relevant conclusions are that while increasing the vertical force increases the potential energy needed at the surface for adsorption, *both* the horizontal elongation force and stiffness decrease the energy needed. This leads to a competition between either horizontal forces or stiffness and vertical forces in the adsorption of a polymer. While we have analysed a directed model of a polymer, it should be noted that when a horizontal force is applied to an isotropic swollen polymer it becomes directed, and so our results should have application to physical two-dimensional systems. Related work on DNA denaturation [33] highlights another possible application of the work on these types of models.

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