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Exact solution for semi-flexible partially directed walks at an adsorbing wall

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Abstract. Recently it was shown that the introduction of stiffness into the model of self-interacting partially directed walks modifies the polymer collapse transition seen from a second-order to a first-order one. Here we consider the effect of stiffness on the adsorption transition. We provide the *exact* generating function for non-interacting semi-flexible partially directed walks and analyse the solution in detail. We demonstrate that stiffness does not change the order of the adsorption transition, in contrast to its effect on collapse.

Keywords: solvable lattice models, classical phase transitions (theory)

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1. Introduction and the model

The phase transitions of an isolated polymer have continued to attract both theoretical and experimental attention; see, for example, [1]–[12]. The adsorption of polymers on a wall, or walls, is one of the key transitions of interest here [13, 2], [14]–[16], [8, 17, 9, 18, 19]. The effect of stiffness, that is the consideration of semi-flexible polymers rather than only fully flexible polymers, has been examined for both exactly solved lattice models [20, 21, 12] and canonical lattice models [22, 23]. In the exactly solved model of interacting partially directed self-avoiding walks (IPDSAW) the addition of stiffness was shown [10, 12] to modify the associated phase transition of polymer collapse from a second-order (tricritical-like) to a first-order one immediately upon application. Here we study the related exactly solvable model for polymer adsorption, namely the partially directed self-avoiding walk (PDW) attached to a sticky wall with the addition of stiffness. The work contained here extends early work [20] on a restricted configuration set. We also note the work on semi-flexible polymer adsorption with a wall in a different orientation [21]. We will consider both enhancing and suppressing bends in the polymer and refer to the model as 'adsorbing semi-flexible partially directed walks' (ASFPDW).

Consider the 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 the walk for $i = 0, 1, \ldots, L$, 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 the $(1, 0)$, $(0, 1)$ and $(0, -1)$ directions 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 in 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; as a result they are often referred to as *tails*. It can also be useful to consider just the walks that are fixed to end on the surface: these are known as *loops*.

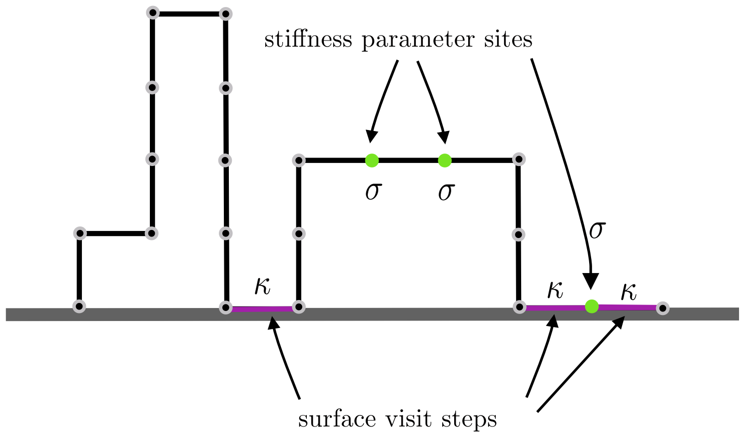

Figure 1. An example of a partially directed walk of length $L = 20$ above a surface, with the parameters κ associated with 'visits' of walk steps to the surface and the stiffness parameter σ associated with the sites (highlighted) between two consecutive horizontal steps. The Boltzmann weight of the configuration shown is $\kappa^3\sigma^3$.

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 adsorption model to mimic the collapse model previously analysed [12]. On the other hand, one may model stiffness by introducing instead a weighting for bends of the walk. Now, the number, b, of bends is equal to $2(N-\ell)$, ignoring end effects, where ℓ is the number of horizontal straight segments. Hence our model is equivalent to one where instead of weighting horizontal straight sections of the walk, bends are weighted with an inverse square weight [24]: the loss of each consecutive straight pair of steps results in the creation of two bends. So considering weighting bends is equivalent to weighting horizontal straight sections and weighting the horizontal length of the walk. When calculating our generating functions below, we include the generalization of a separate weighting of the horizontal length and although the analysis presented does not, for the sake of simplicity, one can see from the form of the generating functions that the conclusions of the paper are not changed when one analyses such a generalization. That is, the weighting of bends rather than horizontal straight segments still does not lead to a change of the order of the adsorption transition. One could also add the stiffness parameter to consecutive vertical steps as well as horizontal steps. The number of such vertical straight segments is equal to $L-b-\ell-1$ and so such a weighting is not independent of the weighting of bends and horizontal straight segments which are themselves related as described above. Hence, likewise the additional weighting of vertical straight segments does not alter the order of the adsorption transition.

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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 $\sigma = \mathrm{e}^{\beta\Delta}$. The polymer partition function $P_L(\kappa)$ for tail configurations of our model is

$$P_L(\kappa,\sigma) = \sum_{\text{tail PDW } \psi_L \text{ of length } L} \kappa^{m(\psi_L)} \sigma^{\ell(\psi_L)}, \tag{1.1}$$

where $m(\psi_L)$ is the number of steps of the walk configuration ψ_L in the surface and $\ell(\psi_L)$ is the number of stiffness sites. We also have the loop partition function $\hat{P}_L(\kappa,\sigma)$, defined similarly. The tail generating function $T(z,\kappa,\sigma)$ is

$$T(z,\kappa,\sigma) = \sum_{L=1}^{\infty} P_L(\kappa,\sigma) z^L, \tag{1.2}$$

while the loop generating function is

$$L(z,\kappa,\sigma) = \sum_{L=1}^{\infty} \hat{P}_L(\kappa,\sigma) z^L. \tag{1.3}$$

In previous work [25] a generating function $G^{(11)}(x,y,\kappa)$ was calculated for the solid-on-solid model related to adsorbing partially directed walks (APDW), where x is associated with the number of horizontal steps N and y with the number of vertical steps $L-N$. So considering walks φ of total length L, number of horizontal steps N and number of steps in the surface m, we define

$$G^{(11)}(x,y,\kappa) = \sum_{\varphi} \kappa^{m(\varphi)} x^{N(\varphi)} y^{L(\varphi)-N(\varphi)}. \tag{1.4}$$

We therefore have

$$T(z,\kappa,1) = G^{(11)}(z,z,\kappa). \tag{1.5}$$

Now, equation (60) in Owczarek and Prellberg [25] gives $G^{(11)}(x,y,\kappa)$ as

$$G^{(11)}(x,y,\kappa) = \frac{x(1-y^2)[(1-\kappa)\Lambda+\kappa]}{(1-x\kappa(1-y^2)-y\Lambda)(1-\Lambda)}, \tag{1.6}$$

with

$$2\Lambda(x,y) = [(1/y+y) - x(1/y-y)] - \left[(1/y-y)^2(1+x^2) - 2x(1/y^2-y^2)\right]^{1/2}. \tag{1.7}$$

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

$$f(\kappa,\sigma) = -\lim_{L\to\infty} \frac{1}{L} \log(P_L(\kappa,\sigma)) \tag{1.8}$$

and is given by

$$f(\kappa,\sigma) = \log z_{\mathrm{s}}(\kappa,\sigma), \tag{1.9}$$

where $z_{\mathrm{s}}(\kappa,\sigma)$ is the closest singularity (on the positive real axis) of the generating function $T(z,\kappa,\sigma)$ in the variable z to the origin.

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The key thermodynamic quantity, $\mathcal{M}$, describing the transition is the average number of steps of the walk located in the surface per step of the walk:

$$\mathcal{M}(\kappa,\sigma) = \lim_{L\to\infty} \left\langle \frac{m}{L} \right\rangle = \lim_{L\to\infty} \frac{\sum_{\psi_L} m(\psi_L)\kappa^{m(\psi_L)}\sigma^{\ell(\psi_L)}}{L\sum_{\psi_L} \kappa^{m(\psi_L)}\sigma^{\ell(\psi_L)}} = \lim_{L\to\infty} \frac{\kappa}{L}\frac{\mathrm{d}\log(P_L(\kappa,\sigma))}{\kappa}, \tag{1.10}$$

which implies

$$\mathcal{M}(\kappa,\sigma) = -\kappa\frac{\mathrm{d}\log z_{\mathrm{s}}(\kappa,\sigma)}{\mathrm{d}\kappa}. \tag{1.11}$$

That is, the variation of z_{s} with κ is directly related to the average occupation of the surface by the walk.

When $\sigma = 1$ one finds that the free energy of tails and loops are the same, and we shall see here that this continues for all σ. When $\sigma = 1$ [13, 25] one finds a single non-analyticity in $z_{\mathrm{s}}(\kappa, 1)$: in fact $z_{\mathrm{s}}(\kappa, 1)$ is constant for small κ, which implies that $\mathcal{M} = 0$, and for κ greater than some transition value, κ_t, it is non-constant. This reflects the existence of an adsorption phase transition which has been well characterized [13, 2]. This adsorption transition can be described as follows: for high temperatures (small κ) the average number of sites m of the walk in the surface is bounded ($\mathcal{M} = 0$) while at low temperatures (large κ) the average number of sites of the walk in the surface is proportional to the length L of the walk ($\mathcal{M} > 0$). We will expect the continuation of this transition for non-unity values of σ, though the question remains of the type of transition. When $\sigma = 1$ the transition is a second-order one with a jump in the specific heat on traversing the transition temperature, and $\mathcal{M}$ vanishing linearly as κ approaches κ_t from above.

2. The solution set-up

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 2. The energy of a configuration is

$$-\beta E(r_0; r_1,\ldots,r_N) = \beta J\sum_{i=1}^{N}\delta_{r_i,0} + \beta\Delta\sum_{j=1}^{N}\delta_{r_{j-1},r_j} \tag{2.1}$$

where we define $r_0 = 0$ for convenience.

Also 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

$$Z_1(r_1) = y^{r_1}\exp(-\beta E(0; r_1)), \tag{2.2}$$

and

$$Z_N(r_N) = \sum_{r_1,\ldots,r_{N-1}\geq 0} y^{L-N}\exp(-\beta E(0; r_1,\ldots,r_N)), \qquad N = 2, 3, \ldots. \tag{2.3}$$

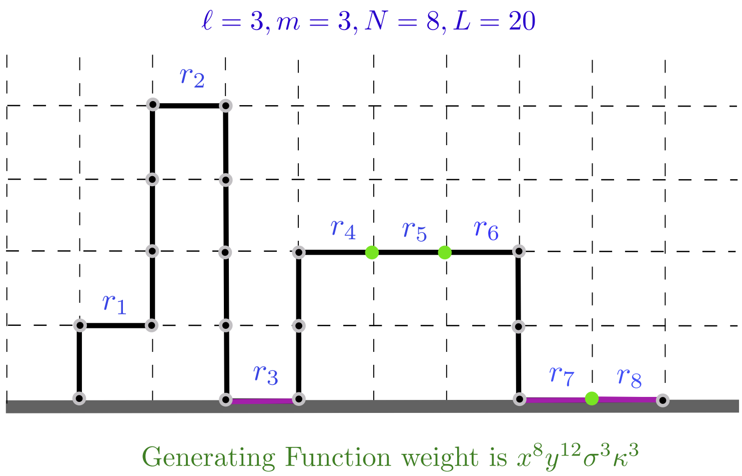

Figure 2. An example of a partially directed walk given by the values of the defining variables r_i, $i = 1, \ldots, 8$. These give the heights of the horizontal steps above the surface: here we have $r_1 = 1, r_2 = 4, r_3 = 0, r_4 = r_5 = r_6 = 2, r_7 = r_8 = 0$. The generating function weight of this configuration is $x^8 y^{12} \kappa^3 \sigma^3$.

We now define the following full generating functions. Firstly, we define the generating function for walks that end at fixed height r as

$$G_r(x, y, \kappa, \sigma) = \sum_{N=1}^{\infty} Z_N(r) x^N, \tag{2.4}$$

and, secondly, the generating function for those ending at any height as

$$G(x, y, \kappa, \sigma) = \sum_{r=0}^{\infty} G_r(x, y, \kappa, \sigma). \tag{2.5}$$

We are interested in finding the tail generating function

$$T(z, \kappa, \sigma) = G(z, z, \kappa, \sigma) \tag{2.6}$$

and the loop generating function

$$L(z, \kappa, \sigma) = G_0(z, z, \kappa, \sigma). \tag{2.7}$$

The first few terms of G_0 and G_1 as series expansions in x are

$$G_0(x, y, q, \kappa) = \kappa x + (\sigma\kappa^2 + \kappa y^2 + \kappa y^4 + \cdots)x^2 + O(x^3) \tag{2.8}$$

and

$$G_1(x, y, q, \kappa) = yx + (y\kappa + y\sigma + y^3 + y^5 + \cdots)x^2 + O(x^3). \tag{2.9}$$

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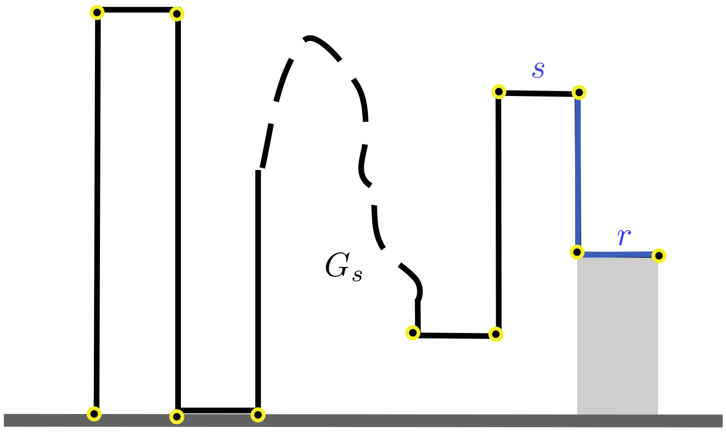

Figure 3. A schematic diagram of the process of adding one column of height r to a configuration ending at height s. The weight factored into the generating function G_s is $xy^{|r-s|}\kappa^{r,0}\sigma^{\delta_{r,s}}$.

3. Exact solution of the generating functions

Using the method in [25] which is based upon the method of Temperley [26], we can find a recursion relation for G_r by the consideration of adding one column of possible steps onto a configuration. One considers any configuration that makes up the generating function G_s and adds a column of height r onto this. It gives a weight factor $xy^{|r-s|}\kappa^{r,0}\sigma^{\delta_{r,s}}$: see figure 3.

Hence, such a concatenation leads to the recursion relation for G_r as follows:

$$G_r = xy^r + x(\sigma-1)G_r + x\sum_{s=0}^{\infty} y^{|r-s|}G_s, \qquad r = 1, \ldots, \tag{3.1}$$

and

$$G_0 = \kappa x + \kappa\sigma x G_0 + \kappa x \sum_{s=1}^{\infty} y^s G_s. \tag{3.2}$$

Note that

$$G = G_0 + \sum_{s=1}^{\infty} G_s. \tag{3.3}$$

Defining

$$u = \frac{x}{1-x(\sigma-1)}, \tag{3.4}$$

$$v = \frac{\kappa(1-x(\sigma-1))}{1-x\kappa(\sigma-1)}, \tag{3.5}$$

and

$$w = \frac{v}{1-vu}, \tag{3.6}$$

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these equations can be rewritten as

$$G_r = uy^r + u\sum_{s=0}^{\infty} y^{|r-s|}G_s, \qquad r = 1, \ldots, \tag{3.7}$$

and

$$G_0 = vu\left(1 + \sum_{s=0}^{\infty} y^s G_s\right). \tag{3.8}$$

The boundary condition can also be written as

$$G_0 = wu\left(1 + \sum_{s=1}^{\infty} y^s G_s\right). \tag{3.9}$$

We point out that for $\sigma = 1$ we have

$$G_r = xy^r + x\sum_{s=0}^{\infty} y^{|r-s|}G_s, \qquad r = 1, \ldots, \tag{3.10}$$

and

$$G_0 = \kappa x\left(1 + \sum_{s=0}^{\infty} y^s G_s\right). \tag{3.11}$$

So x can simply replaced by u and κ by v in (3.10) and (3.11) to give the equations (3.7) and (3.8) when $\sigma \neq 1$.

It will be useful to note that for $r = 1$ we have

$$G_1 = uy + uyG_0 + \frac{u}{y}\sum_{s=1}^{\infty} y^s G_s, \tag{3.12}$$

and so

$$G_1 = uy(1 + wu) + \frac{u}{y}[1 + wuy^2]\sum_{s=1}^{\infty} y^s G_s. \tag{3.13}$$

This becomes the boundary condition that will be useful in solving for the generating functions.

We concentrate first on solving for the G_r for $r \geq 1$ as these obey the same recurrence (3.7). Taking differences in (3.7), we first eliminate the inhomogeneous term,

$$G_{r+1} - yG_r = u(1 - y^2)\left(\frac{1}{y}\right)^{r+1}\sum_{s=r+1}^{\infty} y^s G_s, \qquad r = 1, 2, \ldots. \tag{3.14}$$

Upon taking differences a second time, we are left with

$$G_{r+2} - \left[\left(y + \frac{1}{y}\right) + u\left(y - \frac{1}{y}\right)\right]G_{r+1} + G_r = 0, \qquad r = 1, 2, \ldots. \tag{3.15}$$

Let us define

$$\rho(u, y) = \left(y + \frac{1}{y}\right) + u\left(y - \frac{1}{y}\right) = \frac{1}{y}\left[1 + y^2 - u(1 - y^2)\right]. \tag{3.16}$$

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Substituting the standard ansatz for constant coefficient difference equations of

$$G_r = A\lambda^{r-1} \qquad \text{for } r \geq 1 \tag{3.17}$$

into the recurrence (3.15) one finds the characteristic equation

$$\lambda^2 - \rho(u, y)\lambda + 1 = 0, \tag{3.18}$$

and we nominally have two solutions

$$\lambda_{\pm} = \tfrac{1}{2}\left(\rho \pm \sqrt{\rho^2 - 4}\right). \tag{3.19}$$

By considering the expansion of these one can see that only one is a power series in u and y with positive coefficients. Hence one can deduce that only one contributes to the solution, so we now define

$$\begin{aligned}\lambda &= \tfrac{1}{2}\left(\rho - \sqrt{\rho^2 - 4}\right)\\ &= \frac{1}{2y}\left[1 + y^2 - u(1-y^2) - \sqrt{\left[(1+u^2)(1-y^2) - 2u(1+y^2)\right](1-y^2)}\right]. \end{aligned}\tag{3.20}$$

We note that $\Lambda(x, y) = \lambda(x, y)$ as one would expect. We also note that when $\rho^2 = 4$, so the discriminant is zero, $\lambda = 1$.

Substituting our ansatz into $\sum_{s=1}^{\infty} y^s G_s$ gives

$$\sum_{s=1}^{\infty} y^s G_s = \frac{Ay}{1 - y\lambda}, \tag{3.21}$$

and so on substitution into (3.13) we have

$$A = uy(1 + wu) + u\left[1 + wuy^2\right]\frac{A}{1 - y\lambda}. \tag{3.22}$$

Solving for A gives

$$A = \frac{uy(1 + wu)(1 - y\lambda)}{1 - y\lambda - u\left[1 + wuy^2\right]}. \tag{3.23}$$

Now using (3.9) gives

$$G_0 = wu + wu\frac{A}{1 - y\lambda}. \tag{3.24}$$

On substitution of (3.24) and the ansatz into (3.3) we obtain

$$G = G_0 + \frac{A}{1 - \lambda} = wu + A\left[\frac{wuy(1 - \lambda) + 1 - y\lambda}{(1 - y\lambda)(1 - \lambda)}\right]. \tag{3.25}$$

So using our expression (3.23) for A gives

$$G_0 = wu\left(1 + \frac{uy^2(1 + wu)}{1 - y\lambda - u\left[1 + wuy^2\right]}\right). \tag{3.26}$$

and

$$G = wu + \frac{uy(1 + wu)(1 - y\lambda)}{1 - y\lambda - u\left[1 + wuy^2\right]}\left[\frac{wuy(1 - \lambda) + 1 - y\lambda}{(1 - y\lambda)(1 - \lambda)}\right]. \tag{3.27}$$

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When $\sigma = 1$ then $u = x$, $v = \kappa$ and $w = \kappa/(1-\kappa x)$, and defining

$$d(x,y,\kappa) = (1-y\lambda)(1-\kappa x) - x\left[1-\kappa x+\kappa x y^2\right], \tag{3.28}$$

then

$$G_0 = \frac{\kappa x}{1-\kappa x}\left(1+\frac{xy^2}{d(x,y,\kappa)}\right) \tag{3.29}$$

and

$$G = \frac{\kappa x}{1-\kappa x} + \frac{xy}{d(x,y,\kappa)}\left[\frac{\kappa xy(1-\lambda)+(1-\kappa x)(1-y\lambda)}{(1-\kappa x)(1-\lambda)}\right]. \tag{3.30}$$

After some algebra we have

$$G(x,y,\kappa,1) = \frac{x\left[(1-\lambda)\left[\kappa d(x,y,\kappa)+\kappa x y^2\right]+y(1-\kappa x)(1-y\lambda)\right]}{(1-\kappa x)(1-\lambda)d(x,y,\kappa)}, \tag{3.31}$$

and subsequently

$$G(x,y,\kappa,1) = \frac{x\left[(\kappa+y+\kappa y^2-1)+\lambda(1-y)(1+\kappa x+y-\kappa y+\kappa x y)\right]}{(1-\lambda)d(x,y,\kappa)}. \tag{3.32}$$

Noting that $\lambda = \rho - 1/\lambda$ one can show that indeed

$$G(x,y,\kappa,1) = \frac{x(1-y^2)[(1-\kappa)\lambda(x,y)+\kappa]}{(1-x\kappa(1-y^2)-y\lambda(x,y))(1-\lambda(x,y))}. \tag{3.33}$$

Hence for general σ we have

$$G(x,y,\kappa,\sigma) = \frac{u(1-y^2)[(1-v)\lambda(u,y)+v]}{[1-uv(1-y^2)-y\lambda(u,y)](1-\lambda(u,y))}. \tag{3.34}$$

Similarly, for G_0 we have for $\sigma = 1$ that

$$G_0(x,y,\kappa,1) = \frac{\kappa x(d(x,y,k)+xy^2)}{(1-\kappa x)d(x,y,\kappa)} = \frac{\kappa x(1-y^2)}{1-x\kappa(1-y^2)-y\lambda(x,y)}. \tag{3.35}$$

Hence for general σ

$$G_0(x,y,\kappa,\sigma) = \frac{\kappa u(1-y^2)}{1-uv(1-y^2)-y\lambda(u,y)}. \tag{3.36}$$

We point out that the denominator factor of $[1-uv(1-y^2)-y\lambda(u,y)]$ is common to both G and G_0. It is this commonality that ensures the equality of the free energy for loops and trails since it is this factor that determines the location of the singularities of both generating functions.

4. Analysis of the phase diagram

4.1. The fully flexible case ($\Delta = 0$)

For the sake of comparison (previous analysis has not been presented in a similar fashion) we review the analysis of the fully flexible case when $\sigma = 1$. When $\sigma = 1$ the generating function for tails is

$$T(z,\kappa) = \frac{z(1-z^2)[(1-\kappa)\lambda+\kappa]}{[1-z\kappa(1-z^2)-z\lambda](1-\lambda)}, \tag{4.1}$$

and for loops it is

$$L(z,\kappa) = \frac{z(1-z^2)}{1-z\kappa(1-z^2)-z\lambda}, \tag{4.2}$$

with

$$2z\lambda(z) = \left[(1-z+z^2+z^3)\right] - \left[(1-2z-z^2)(1-z^4)\right]^{1/2}. \tag{4.3}$$

We wish to find the singularity closest to the origin $z_{\mathrm{s}}(\kappa, 1)$. There are two relevant singularities in the generating functions. One occurs when the argument of the square root in λ (discriminant) is zero:

$$(1-2z-z^2)(1-z^4) = 0, \tag{4.4}$$

the one closest to the origin being

$$z = \sqrt{2} - 1 \equiv z_{\mathrm{d}}, \tag{4.5}$$

which also implies that $\lambda = 1$; and another when the other factor in the denominator is zero, that is,

$$D(z,\kappa) \equiv 1 - z\kappa(1-z^2) - z\lambda = 0. \tag{4.6}$$

Let us refer to this second singularity as $z_{\mathrm{a}}(\kappa)$ (or more generally $z_{\mathrm{a}}(\kappa, \sigma)$) given implicitly by

$$\kappa = \frac{1-z\lambda(z)}{z(1-z^2)}. \tag{4.7}$$

The change from one singularity to the other defines the transition binding strength of $\kappa_t(1)$. The two singularities occur simultaneously when $\lambda = 1$ and $z = z_{\mathrm{d}}$ giving from (4.7)

$$\kappa = \kappa_t(1) = \frac{1}{z_{\mathrm{d}}(1+z_{\mathrm{d}})} = 1 + \frac{1}{\sqrt{2}}. \tag{4.8}$$

There is no solution to the equation (4.7) in the range $|z| \leq z_{\mathrm{d}}$ for $0 < \kappa < \kappa_t$. So the second singularity only occurs when $\kappa \geq \kappa_t$. Hence we have

$$z_{\mathrm{s}}(\kappa,1) = \begin{cases} \sqrt{2}-1 & 0 \leq \kappa \leq \kappa_t(1) \\ z_{\mathrm{a}}(\kappa) & \kappa \geq \kappa_t(1). \end{cases} \tag{4.9}$$

Now

$$\lambda = 1 - c_1\sqrt{(z_{\mathrm{d}}-z)} + O((z_{\mathrm{d}}-z)). \tag{4.10}$$

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By expanding $D(z,\kappa)$ about $z = z_{\mathrm{d}}$ and $\kappa = \kappa_t$, assuming $z < z_{\mathrm{d}}$ and $\kappa > \kappa_t$ one finds

$$D(z,\kappa) = (2\sqrt{2}-2)\sqrt{(z_{\mathrm{d}}-z)} - (6-4\sqrt{2})(\kappa-\kappa_t) + O(z_{\mathrm{d}}-z) + ((\kappa-\kappa_t)^2). \tag{4.11}$$

Hence, for $\kappa \approx \kappa_t$ with $\kappa > \kappa_t$ we have

$$z_{\mathrm{a}} = z_{\mathrm{d}} - c_2(\kappa-\kappa_{\mathrm{d}})^2 + O((\kappa-\kappa_{\mathrm{d}})^3). \tag{4.12}$$

Since $z_{\mathrm{s}} = z_{\mathrm{d}}$ for $\kappa < \kappa_t$ this implies that the specific heat exponent $\alpha = 2$, that is, the adsorption transition is a second-order one.

When $\lambda \to 1$ we have $1-\lambda \sim c_1\sqrt{(z_{\mathrm{d}}-z)}$. For $\kappa < \kappa_t$ the generating function G_0 has a convergent square root singularity at z_{d} while G has a divergent square root singularity at z_{d}. For $\kappa > \kappa_t$ both generating functions have simple poles at z_{a} since $D(z,\kappa)$ has a simple zero. For $\kappa = \kappa_t$ we have $D(z,\kappa_t) \sim c_3\sqrt{(z_{\mathrm{d}}-z)}$ and so the generating function G_0 has a divergent square root singularity while G has a simple pole.

4.2. Semi-flexible polymers: the solution when $\Delta \neq 0$

For general σ the generating function for tails is

$$T(z,\kappa,\sigma) = \frac{u(1-z^2)[(1-v)\lambda+v]}{[1-uv(1-z^2)-z\lambda](1-\lambda)}, \tag{4.13}$$

and for loops it is

$$L(z,\kappa,\sigma) = \frac{vu(1-z^2)}{1-uv(1-z^2)-z\lambda}, \tag{4.14}$$

with

$$u = \frac{z}{1-z(\sigma-1)}, \tag{4.15}$$

$$v = \frac{\kappa(1-z(\sigma-1))}{1-z\kappa(\sigma-1)}, \tag{4.16}$$

and

$$\lambda = \frac{1}{2z}\left[1+z^2-u(1-z^2)-\sqrt{[(1-z^2)(1+u^2)-2u(1+z^2)]\,(1-z^2)}\right]. \tag{4.17}$$

The algebraic singularity arising from λ occurs when the discriminant is zero at $z = z_{\mathrm{d}}$: namely, at

$$\left([1-(\sigma-1)z_{\mathrm{d}}]^2 + z_{\mathrm{d}}^2\right)(1-z_{\mathrm{d}}^2) - 2z_{\mathrm{d}}(1+z_{\mathrm{d}}^2)(1-(\sigma-1)z_{\mathrm{d}}) = 0. \tag{4.18}$$

This can be factorized to show that the singularity obeys

$$1-(\sigma+1)z_{\mathrm{d}} + (\sigma-2)z_{\mathrm{d}}^2 = 0. \tag{4.19}$$

This gives

$$z_{\mathrm{d}}(\sigma) = \frac{1+\sigma-\sqrt{9-2\sigma+\sigma^2}}{2(\sigma-2)}. \tag{4.20}$$

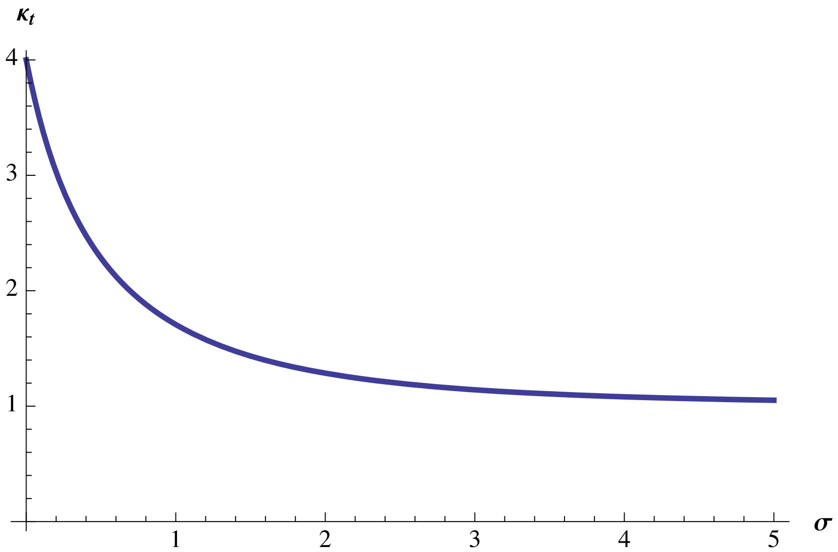

Figure 4. A plot of $\kappa_t(\sigma)$ against σ.

One can readily discover that the solution $z_{\rm d}(\sigma)$ is a monotonically decreasing function of σ with

$$z_{\rm d} = \begin{cases} 1/2 & \sigma = 0 \\ \sqrt{2}-1 & \sigma = 1 \\ 1/3 & \sigma = 2 \\ \to 1/\sigma & \sigma \to \infty. \end{cases} \tag{4.21}$$

It is important to realize that $\lambda(u(z_{\rm d},\sigma), z_{\rm d}) = 1$. Also note that $\sigma z_{\rm d}$ increases with σ.

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

$$1 - uv(1-z^2) - z\lambda = (1-z\lambda)(1-z\kappa(\sigma-1)) - \kappa z(1-z^2) = 0, \tag{4.22}$$

that is,

$$\kappa = \frac{(1-z\lambda)}{z(1-z^2) + (\sigma-1)z(1-z\lambda)} \tag{4.23}$$

gives $z = z_{\rm a}(\kappa,\sigma)$ (the 'adsorbed' singularity) implicitly.

The two singularities coincide when $z_{\rm a} = z_{\rm d}$, that is,

$$\kappa_t(\sigma) = \frac{1}{\sigma z_{\rm d} + z_{\rm d}^2} = \frac{4(\sigma-2)^2}{[1+\sigma-\sqrt{9+\sigma(\sigma-2)}][1+(2\sigma-3)\sigma-\sqrt{9+\sigma(\sigma-2)}]}. \tag{4.24}$$

A plot of $\kappa_t(\sigma)$ can be found in figure 4.

For example, some numerical values are

$$\kappa_t(\sigma) = \begin{cases} 4 & \sigma = 0 \\ 1+1/\sqrt{2} & \sigma = 1 \\ 9/7 & \sigma = 2 \\ \to 1 & \sigma \to \infty. \end{cases} \tag{4.25}$$

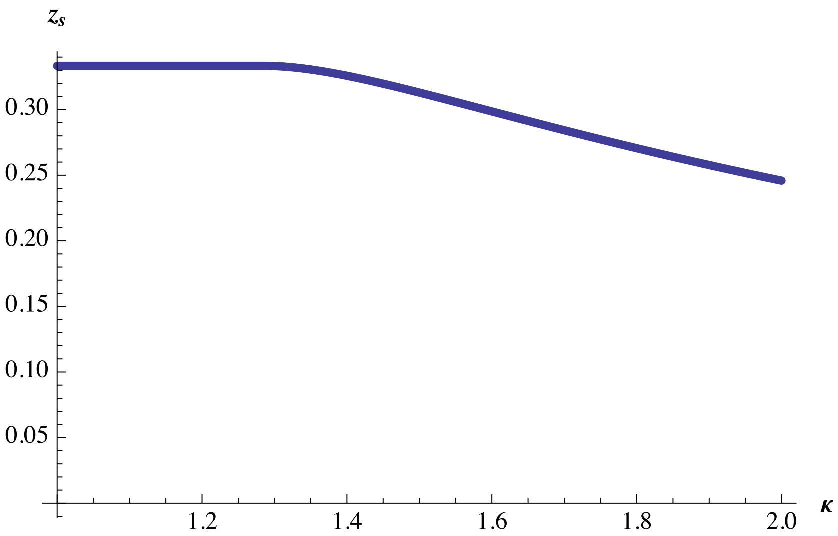

Figure 5. A plot of z_s against κ for $\sigma = 2$. The desorbed constant value of $z_s = z_d = 1/3$. The transition occurs at $\kappa = 9/7 \approx 1.28$.

The function $\kappa_t(\sigma)$ is a monotonically decreasing function of σ. Hence the transition temperature increases with increasing stiffness: it is easier to adsorb stiff polymers. As an aside it should be stressed that $\kappa_t(\sigma)$ is an analytic function of σ for real σ including at $\sigma = 2$.

Once again the adsorbed singularity only occurs when $\kappa \geq \kappa_t$ and for $\kappa > \kappa_t$ it is the singularity closest to the origin. In figure 5 $z_s(\kappa, 2)$ is plotted against κ: the transition at $\kappa = 9/7 \approx 1.28$ is visible.

Because λ once again has an expansion

$$\lambda = 1 - c\sqrt{(z_d - z)} + O((z_d - z)) \tag{4.26}$$

the nature of the crossover from one singularity to the other remains unchanged when $\sigma \neq 1$. Hence the transition remains a second-order one.

The types of singularity in generating functions in the regimes $\kappa < \kappa_t$, $\kappa = \kappa_t$ and $\kappa > \kappa_t$ are the same as in the case $\sigma = 1$.

5. Conclusions

We have solved exactly a model of semi-flexible polymers absorbing onto a sticky surface in two dimensions. We have shown that stiffness does not affect the order of the transition, in contrast to the collapse transition case, where the addition of stiffness changes the transition from a second-order one to a first-order one. We have demonstrated, in accord with expectations, that increasing stiffness increases the adsorption temperature.

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