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A self-interacting partially directed walk subject to a force

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Abstract
We consider a directed walk model of a homopolymer (in two dimensions) which is self-interacting and can undergo a collapse transition, subject to an applied tensile force. We review and interpret all the results already in the literature concerning the case where this force is in the preferred direction of the walk. We consider the force extension curves at different temperatures as well as the critical-force temperature curve. We demonstrate that this model can be analysed rigorously for all key quantities of interest even when there may not be explicit expressions for these quantities available. We show which of the techniques available can be extended to the full model, where the force has components in the preferred direction and the direction perpendicular to this. Whilst the solution of the generating function is available, its analysis is far more complicated and not all the rigorous techniques are available. However, many results can be extracted including the location of the critical point which gives the general critical-force temperature curve. Lastly, we generalize the model to a three-dimensional analogue and show that several key properties can be analysed if the force is restricted to the plane of preferred directions.

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

1. Introduction

The development of atomic force microscopy and optical tweezers has allowed experimentalists to micro-manipulate individual polymer molecules (e.g., Bemis *et al* (1999), Haupt *et al* (2002), Gunari *et al* (2007)), and this has led to a considerable body of theoretical work describing the response of a polymer to an applied force (e.g., Halperin and Zhulina (1991), Cooke and Williams (2003), Rosa *et al* (2003)). Several situations have been investigated, including pulling a polymer off a surface at which it is adsorbed, pulling a polymer from a preferred solvent to a less preferred solvent, pulling a copolymer which is localized at an interface between two immiscible liquids and pulling a collapsed polymer (in a poor solvent) to an extended form. In this paper we shall be concerned with the latter problem.

The stress–strain curve of a linear polymer in a poor solvent, being pulled in an AFM experiment, has been measured by several groups (Haupt *et al* 2002, Gunari *et al* 2007). The force–extension curve shows a characteristic plateau. For forces below this critical value the polymer will be in a collapsed state, while for forces above the critical value the polymer will be stretched. The plateau region would seem to indicate a first-order phase transition. Indeed Grassberger and Hsu (2002) have studied self-avoiding walks with nearest-neighbour attraction and an applied force at low temperatures (poor solvents): they predicted a first-order phase transition in three dimensions. On the other hand, they see no sign of a first-order transition in two dimensions.

A well-studied exactly solved model of poor solvent polymers is the self-interacting partially directed self-avoiding walk model (IPDSAW). We begin our discussion by noting that a partially directed self-avoiding walk on the square lattice without self-interaction is intrinsically anisotropic with a preferred direction so that the polymer's size scales proportionally to its length, and one perpendicular to this so that the polymer's size in this direction scales sub-linearly. As we shall consider the square lattice with the polymer oriented one way, the preferred direction will be the *horizontal* direction and the other direction will be the *vertical* direction.

In the absence of an applied force the critical point of this model was found by Binder *et al* (1990), and is expected to model the polymer collapse transition (or θ-point). The exact solution of the generating function was found by Brak *et al* (1992) and its singularity structure was rigorously elucidated. Prellberg *et al* (1993) used recurrence relations to generate very long series to estimate the exponents and the scaling function for the phase transition. A second-order phase transition similar to the θ-point was found. The tricritical nature of this transition was described by Owczarek *et al* (1993) based upon small parameter expansions and calculations of a related version of the model (see below).

Various calculations were made by Owczarek *et al* (1993) that are worth noting. First a semi-continuous version of the model was solved explicitly, building on works by Zwanzig and Lauritzen (1968, 1970) on a related model, and showed the same tricritical nature (identical exponents) as the lattice model (from the small parameter expansion and the numerical work of Prellberg *et al* (1993)). A later calculation by Prellberg (1995) on the asymptotics of the generating function of the lattice model of staircase polygons enumerated by perimeter and area implicitly demonstrated that the scaling function and the exponents were also the same as in the fully discrete model: the q-Bessel functions involved are the same in the two lattice models. This was made explicit recently by Owczarek and Prellberg (2007). The low temperature scaling of the partition function was found by Owczarek (1993) in the semi-continuous model, and once again this was the same as found by Prellberg *et al* (1993) numerically for the fully discrete case. We argue below that the uniform asymptotic expansion given by Owczarek and Prellberg (2007) implies that they are indeed similar.

Second, Owczarek *et al* (1993) generalized the fully discrete model to include a parameter that counts the horizontal span of the walks. The generating function was found by generalizing the approach of Brak *et al* (1992) for the no-force case. This added parameter is equivalent to considering a force applied in the preferred direction. The semi-continuous model also contained this parameter. In the semi-continuous model it was clear that this parameter did not change the nature of the transition. In the discrete model it was also implicit that the collapse transition was unchanged by this parameter (and confirmed by the work of Prellberg (1995)), and so unchanged by such an applied force. The connection to an applied force was however not made explicit in the paper. Rosa *et al* (2003) studied the model numerically with the connection made explicit, and added the consideration of the end-to-end distance scaling function for the discrete model, corroborating the unchanged tricritical nature of the transition when an applied force in the preferred direction is added. They also plotted the critical-force-against-temperature curve for the discrete and semi-continuous models. Again the work of Owczarek and Prellberg (2007) makes this conclusion explicit.

Third, in the appendix of Owczarek *et al* (1993) a further generalization of the model was considered and the full generating function of this further generalization evaluated exactly. In this generalization the parameter for vertical steps was replaced by two parameters: one for steps in the positive vertical direction and one for steps in the negative vertical direction. No analysis of this generating function was attempted. We note that a recent paper by Kumar and Giri (2007) considered pulling in both directions though their focus was on finite size effects calculated numerically rather than thermodynamic transitions and exact results.

In this paper we make explicit the connection to applying a force in the vertical (non-preferred) direction of the generalization discussed above. However, we go further and solve for the generating function along the surface in the parameter space which should include the transition point. Hence we find an explicit expression for the phase transition point and so are able to plot exactly the critical force against temperature curve. We also observe that one of the tricritical exponents is unchanged when this non-preferred force is applied. This indicates, though does not prove, that the transition may remain second order even in the case of this type of force. This is a little unexpected as the force must change the end-to-end scaling of the high temperature phase when pulling in the vertical direction from sub-linear to linear, which it does not when applied in the horizontal direction.

We also derive functional equations for the generating function and show how the solution of this general class of problem can be streamlined with this approach.

Before we explain our work on the vertical pulling problem we summarize all the known results on the horizontal pulling problem making explicit the results in terms of the applied force. Moreover, we apply the rigorous techniques of Brak *et al* (1992), which had only been applied to the case of no applied force, to the horizontal pulling problem. In addition we discuss the behaviour of the force–extension curves based upon the exact results. Essentially we bring together all the known results and extend them as necessary for the case of horizontal pulling of a partially directed polymer in two dimensions.

At the end of this paper we consider a three-dimensional analogue of the model and show it has similar behaviour to its two-dimensional counterparts.

2. Model and definitions

Consider the square lattice and a self-avoiding walk that has one end fixed at the origin on that lattice. 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 (PDSAW). For convenience, we consider walks that have their first step in the horizontal direction. Let the total number of steps in the walk be n. We label the vertices of the walk $i = 0, 1, 2, \ldots, n$. Let the number of horizontal steps be n_x and the number of vertical steps be n_y. To define our model we will need finer definitions, so let us define n_{y_+} to be the number of $(0, 1)$ steps (positive vertical steps) and n_{y_-} to be the number of $(0, -1)$ steps (negative vertical steps). If the walk starts at the origin

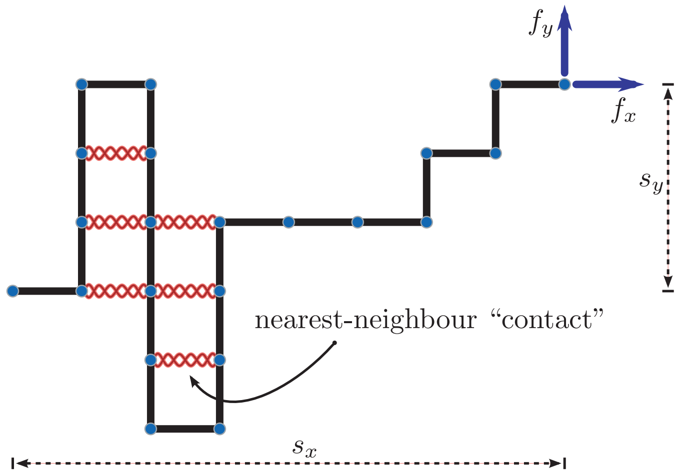


Figure 1. An example of a partially directed walk (the bold black path) of length $n = 21$ with $n_x = 8$, $n_{y_+} = 8$, and $n_{y_-} = 5$ and having six nearest-neighbour 'contacts' (shown as intertwined (red) curves) so $m = 6$. The horizontal span is $s_x = 8$, while the vertical span is $s_y = 3$. One end is fixed at the origin, while forces are applied to the other end (horizontal f_x and vertical f_y).

let the position of the other end-point be (s_x, s_y) so that the *span* in the horizontal direction is s_x and the *span* of the walk in the vertical direction is s_y. We therefore have

$$\begin{aligned} n &= n_x + n_y \\ &= n_x + n_{y_+} + n_{y_-} \end{aligned} \tag{2.1}$$

and

$$\begin{aligned} s_x &= n_x \\ s_y &= n_{y_+} - n_{y_-}. \end{aligned} \tag{2.2}$$

An example configuration along with the associated variables of our model is illustrated in figure 1.

To define our model we add various energies and hence Boltzmann weights to the walk. First, any two occupied sites of the walk not adjacent in the walk though adjacent on the lattice are denoted *nearest-neighbour contacts* or *contacts*: see figure 1. An energy $-J$ is added for each such contact. We define a Boltzmann weight $\omega = \mathrm{e}^{\beta J}$ associated with these contacts, where $\beta = 1/k_B T$ and T is the absolute temperature. Without loss of generality we shall take the units of energy to be such that $J = 1$ and therefore $\omega = \mathrm{e}^{\beta}$, except when we discuss pulling polymers without any self-interaction ($\omega = 1$) where we will have $J = 0$.

An external horizontal force f_x pulling at the other end of the walk adds a Boltzmann weight h^{s_x} with $h = \mathrm{e}^{\beta f_x}$. An external vertical force f_y pulling at the other end of the walk adds a Boltzmann weight v^{s_y} with $v = \mathrm{e}^{\beta f_y}$.

The partition function $Z_n(f_x, f_y, \beta)$ of the model for walks of length $n \geqslant 1$, where for later mathematical convenience the first step of the walk is a horizontal step, is

$$Z_n(f_x, f_y, \beta) = \sum_{\varphi \text{ is PDSAW of length } n} h^{s_x(\varphi)} v^{s_y(\varphi)} \omega^{m(\varphi)}, \tag{2.3}$$

where $m(\varphi)$ is the number of nearest-neighbour contacts in the PDSAW, φ. The generating function $\hat{G}(z; h, v, \omega)$ is

$$\hat{G}(z; h, v, \omega) = \sum_{n=1}^{\infty} Z_n(f_x, f_y, \beta) z^n, \tag{2.4}$$

so z can be considered as a fugacity for the steps of the walk and the generating function as a 'generalized partition function'. We shall denote the radius of convergence of $\hat{G}(z; h, v, \omega)$ as a function of z as $z_c(h, v, \omega)$. The mean values of n, m, s_x and s_y are given by

$$\begin{aligned} \langle n \rangle &= z \frac{\partial \log \hat{G}}{\partial z}, \qquad & \langle m \rangle &= \omega \frac{\partial \log \hat{G}}{\partial \omega}, \\ \langle s_x \rangle &= h \frac{\partial \log \hat{G}}{\partial h}, \qquad & \langle s_y \rangle &= v \frac{\partial \log \hat{G}}{\partial v}. \end{aligned} \tag{2.5}$$

We shall define the number of n-edge partially directed walks with m nearest-neighbour contacts, horizontal span s_x and vertical span s_y as $d_n(s_x, s_y, m)$ so that

$$Z_n(f_x, f_y, \beta) = \sum_{s_x, s_y, m} d_n(s_x, s_y, m) h^{s_x} v^{s_y} \omega^m. \tag{2.6}$$

When $v = 1$, that is $f_y = 0$, we let

$$b_n(s_x, m) = \sum_{s_y} d_n(s_x, s_y, m), \tag{2.7}$$

and so $b_n(s_x, m)$ is the number of n-edge partially directed walks with m nearest-neighbour contacts and horizontal span s_x. So

$$Z_n(f_x, 0, \beta) = \sum_{s_x, m} b_n(s_x, m) h^{s_x} \omega^m. \tag{2.8}$$

Let the number of partially directed walks of length n be $\bar{b}_n$ so that

$$\bar{b}_n = \sum_{s_x, s_y, m} d_n(s_x, s_y, m) = \sum_{s_x, m} b_n(s_x, m). \tag{2.9}$$

It is advantageous when working with the generating function to define different variables. Let the generating function $G(x, y_+, y_-, \omega)$ be defined as

$$G(x, y_+, y_-, \omega) = \sum_{n=1}^{\infty} \sum_{\varphi} x^{n_x(\varphi)} {y_+}^{n_{y+}(\varphi)} {y_-}^{n_{y-}(\varphi)} \omega^{m(\varphi)}, \tag{2.10}$$

where the sum over φ is over all PDSAWs of length n. Then making the substitutions

$$\begin{aligned} x &= hz \\ y_+ &= vz \\ y_- &= z/v \end{aligned} \tag{2.11}$$

demonstrates that

$$G(hz, zv, z/v, \omega) = \hat{G}(z; h, v, \omega). \tag{2.12}$$

Hence we have

$$\begin{aligned} Z_n(f_x, f_y, \beta) &= [z^n] G(hz, zv, z/v, \omega) \\ &= \frac{1}{2\pi \mathrm{i}} \oint G(hz, zv, z/v, \omega) \frac{\mathrm{d}z}{z^{n+1}}. \end{aligned} \tag{2.13}$$

It will be useful to define

$$q_+ = y_+\omega \qquad \text{and} \qquad q_- = y_-\omega \tag{2.14}$$

and

$$q = \sqrt{q_+q_-}, \tag{2.15}$$

and on making the substitutions (2.11)

$$q = \omega z. \tag{2.16}$$

We define the reduced limiting free energy as

$$\kappa(f_x, f_y, \beta) = \lim_{n\to\infty} \frac{1}{n} \log[Z_n(f_x, f_y, \beta)] \tag{2.17}$$

where the existence of the limit can be established by concatenation arguments. The radius of convergence $z_c(h, v, \omega)$ can be related to the free energy $\kappa(f_x, f_y, \beta)$ as

$$\kappa(f_x, f_y, \beta) = -\log z_c(h, v, \omega). \tag{2.18}$$

It will turn out that there is a single phase transition where the free energy is singular as a function of β. We shall denote the phase-transition inverse-temperature as $\beta^t \equiv \beta^t(f_x, f_y)$. In general a superscript of t implies the critical value of a parameter, e.g., the critical horizontal force at a fixed temperature and zero vertical force is $f_x^t \equiv f_x^t(0, \beta)$. However, we use a subscript t to denote the critical values of the fugacities. The value of the radius of convergence of $\hat{G}(z; h, v, \omega)$ as a function of z at $\omega_t = e^{\beta^t}$ is $z_c^t(h, v) = z_c(h, v, \omega_t(h, v))$.

When $f_y = 0$ we shall set $y = y_+ = y_-$ and so the generating function we need to consider for the case where there is no vertical stretching force is $G(x, y, y, \omega)$, noting that $G(hz, z, z, \omega) = \hat{G}(z; h, 1, \omega)$, where

$$\hat{G}(z; h, 1, \omega) = \sum_{n=1}^{\infty} Z_n(f_x, 0, \beta) z^n = \sum_{n, s_x, m} b_n(s_x, m) h^{s_x} \omega^m z^n. \tag{2.19}$$

Note that for $f_y = 0$ we have

$$q = y\omega, \tag{2.20}$$

which agrees with (2.16) when the substitutions (2.11) are made since $y = z$ when $y = y_+ = y_-$ (that is, $v = 1$).

In subsequent calculations it is convenient to define the generating function $G_r(x, y_+, y_-, \omega)$ for walks that have r vertical steps immediately after the first horizontal step, where $-\infty < r < \infty$. It will also be convenient to introduce the generating function $G_r^+(x, y_+, y_-, \omega) = G_r(x, y_+, y_-, \omega)$ for walks that have $r \geqslant 0$ steps after the first horizontal step in the positive y-direction and $G_r^-(x, y_+, y_-, \omega) = G_{-r}(x, y_+, y_-, \omega)$ that have $r \geqslant 0$ steps after the first horizontal step in the negative y-direction. Clearly, $G_0^+ = G_0^-$.

In the functional equation section (section 7) we need

$$F(p) = \sum_{r=-\infty}^{\infty} G_r(x, y, y, \omega) p^r, \tag{2.21}$$

$$F^+(p) = \sum_{r=0}^{\infty} G_r^+(x, y_+, y_-, \omega) p^r \tag{2.22}$$

and

$$F^-(p) = \sum_{r=1}^{\infty} G_r^-(x, y_+, y_-, \omega) p^r. \tag{2.23}$$

Note the asymmetry of the summation index in the final two definitions. Note that

$$G(x, y, y, \omega) = F(1) = \sum_{r=-\infty}^{\infty} G_r(x, y, \omega) \tag{2.24}$$

and

$$G(x, y_+, y_-, \omega) = F^+(1) + F^-(1) = \sum_{r=-\infty}^{\infty} G_r(x, y_+, y_-, \omega). \tag{2.25}$$

3. Pulling in the preferred direction ($f_y = 0$)

In this section we will begin discussing the case of horizontal pulling force where $f_y = 0$.

3.1. No self-interactions ($\omega = 1$)

Let us begin by considering the case of no interactions and no force so that $J = f_x = f_y = 0$. It is easy to see that $\lim_{n\to\infty} n^{-1} \log \bar{b}_n = \log(1 + \sqrt{2})$. Let us consider the case of no vertical force so that $f_y = 0$ and $v = 1$. As discussed in the previous section we are interested in the generating function $\hat{G}(z; h, 1, \omega) = G(hz, z, z, \omega)$. As defined above this generating function converges when $z < z_c(h, 1, \omega)$. Recall that the free energy $\kappa(f_x, 0, \beta)$ is given by $\kappa = -\log z_c$ (assuming that the limit defining the free energy exists, which will be proved in a later section).

When $\omega = 1$ (which corresponds to turning off the vertex–vertex interaction and hence to good solvent conditions), $\hat{G}(z; 1, h, 1)$ satisfies the equation

$$\hat{G}(z; h, 1, 1) = hz(1 + \hat{G}(z; h, 1, 1)) + \frac{2hz^2}{1-z}(1 + \hat{G}(z; h, 1, 1)), \tag{3.1}$$

so that

$$1 + \hat{G}(z; h, 1, 1) = \frac{1-z}{1 - z - hz - hz^2}. \tag{3.2}$$

From this we can readily calculate the ratio $\langle s_x\rangle/\langle n\rangle$ and take the thermodynamic limit by letting $z \to z_c(h, 1, 1)$ where

$$z_c(h, 1, 1) = \frac{\sqrt{h^2 + 6h + 1} - 1 - h}{2h}. \tag{3.3}$$

In figure 2 is a plot of $\lim_{z\to z_c} \langle s_x\rangle/\langle n\rangle$ against βf_x. Note that the stress–strain curve is qualitatively the same as that found experimentally for polystyrene in a good solvent (toluene) (Gunari *et al* 2007, figure 1).

For $\omega \neq 1$ the situation is more difficult and we derive some results about the generating function in the following sections.

3.2. Convexity and continuity for $\omega \neq 1$

In this section we establish the existence of the thermodynamic limit for the canonical problem, and prove convexity and continuity. This implies continuity of the phase boundary.

It will be convenient to consider a subset of the walks counted by $\hat{G}(z; h, 1, \omega)$. Let $a_n(s_x, m)$ be the number of partially directed walks with n edges, m contacts and x-span equal to s_x which satisfy the additional constraint that their last step is in the east direction. (That is, both the first and last steps are east steps.) These walks can be concatenated by

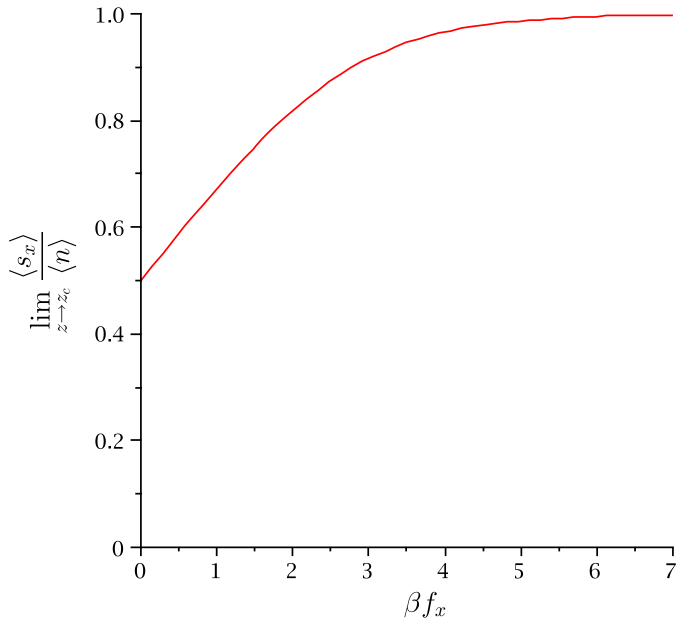


Figure 2. The dependence of $\lim_{z\to z_c} \langle s_x\rangle/\langle n\rangle$ on βf_x when $\omega = 1$.

identifying the last vertex of one walk with the first vertex of the other walk which yields the inequality

$$a_{n_1+n_2}(s_x, m) \geqslant \sum_{s_{x_1}, m_1} a_{n_1}(s_{x_1}, m_1) a_{n_2}(s_x - s_{x_1}, m - m_1). \tag{3.4}$$

Defining the partition function

$$A_n(h, \omega) = \sum_{s_x, m} a_n(s_x, m) h^{s_x} \omega^m, \tag{3.5}$$

this implies the super-multiplicative inequality

$$A_{n_1+n_2}(h, \omega) \geqslant A_{n_1}(h, \omega) A_{n_2}(h, \omega). \tag{3.6}$$

Since $A_n(h, \omega) \leqslant 3^n \omega^n h^n$, it follows that $n^{-1} \log A_n(h, \omega)$ is bounded above for $h, \omega < \infty$. Hence the super-multiplicative inequality above implies the existence of the limit

$$\lim_{n\to\infty} n^{-1} \log A_n(h, \omega) \equiv \tilde{\kappa}(f_x, \beta) \tag{3.7}$$

for $h, \omega < \infty$.

We now recall the definition of the partition function

$$Z_n(f_x, 0, \beta) = \sum_{m, s_x} b_n(m, s_x) \omega^m h^{s_x} \tag{3.8}$$

and define $B_n(h, \omega) = Z_n(f_x, 0, \beta)$. Since $A_{n+1}(h, \omega) = h B_n(h, \omega)$ it follows that

$$\lim_{n\to\infty} n^{-1} \log B_n(h, \omega) = \tilde{\kappa}(f_x, \beta) = \kappa(f_x, 0, \beta) \tag{3.9}$$

for $h, \omega < \infty$.

To prove that $\kappa(f_x, \beta)$ is a convex function of β and βf_x we note that Hölder's inequality implies that

$$\left(\sum_{m,s_x} b_n(m,s_x)\omega_1^m h_1^{s_x}\right)\left(\sum_{m,s_x} b_n(m,s_x)\omega_2^m h_2^{s_x}\right) \geqslant \left(\sum_{m,s_x} b_n(m,s_x)(\sqrt{\omega_1\omega_2})^m(\sqrt{h_1h_2})^{s_x}\right)^2 \tag{3.10}$$

so that

$$B_n(h_1,\omega_1)B_n(h_2,\omega_2) \geqslant B_n(\sqrt{\omega_1\omega_2}, \sqrt{h_1h_2})^2 \tag{3.11}$$

and hence

$$\frac{n^{-1}\log B_n(h_1,\omega_1) + n^{-1}\log B_n(h_2,\omega_2)}{2} \geqslant n^{-1}\log B_n(\sqrt{h_1h_2}, \sqrt{\omega_1\omega_2}). \tag{3.12}$$

This shows that $n^{-1}\log B_n(h,\omega)$ is a convex function of β and βf_x. (It is convex as a surface, not just separately convex in each variable.) Since the limit of a sequence of convex functions (when it exists) is a convex function, $\kappa(f_x, 0, \beta)$ is a convex function of β and βf_x. Hence $\kappa(f_x, 0, \beta)$ is continuous and differentiable almost everywhere. Since $\kappa(f_x, 0, \beta) = -\log z_c(h, 1, \omega)$, the singularity surface $z = z_c(h, 1, \omega)$ is also continuous and differentiable almost everywhere.

3.3. The generating function for $\omega \neq 1$

While the calculation of the generating function for $\omega \neq 1$ appears in Owczarek *et al* (1993) (see section 4 of that paper) we feel that it is worth summarizing and presenting in a slightly different way. In order to consider the case $\omega \neq 1$ it was necessary to generalize a method originally due to Temperley (1956) and used for the case $h = 1$ by Brak *et al* (1992).

For convenience let the partial generating function $\hat{G}_r(z; h, 1, \omega)$ in the case where $v = 1$ (no vertical force) be denoted as

$$g_r = 2\hat{G}_r(z; h, 1, \omega) \qquad r \geqslant 1, \tag{3.13}$$

and $g_0 = \hat{G}_0(z; h, 1, \omega)$. Now the generating function required is $\hat{G}(z; h, 1, \omega)$ which is the sum over all r as

$$\hat{G}(z; h, 1, \omega) = \sum_{r=-\infty}^{\infty} \hat{G}_r(z; h, 1, \omega). \tag{3.14}$$

Noting that $\hat{G}_{-r}(z; h, 1, \omega) = \hat{G}_r(z; h, 1, \omega)$, we have the partial generating functions g_r satisfying the relations

$$g_0 = hz + hz(g_0 + g_1 + \cdots) = hz(1 + \hat{G}(z; h, 1, \omega)) \tag{3.15}$$

and

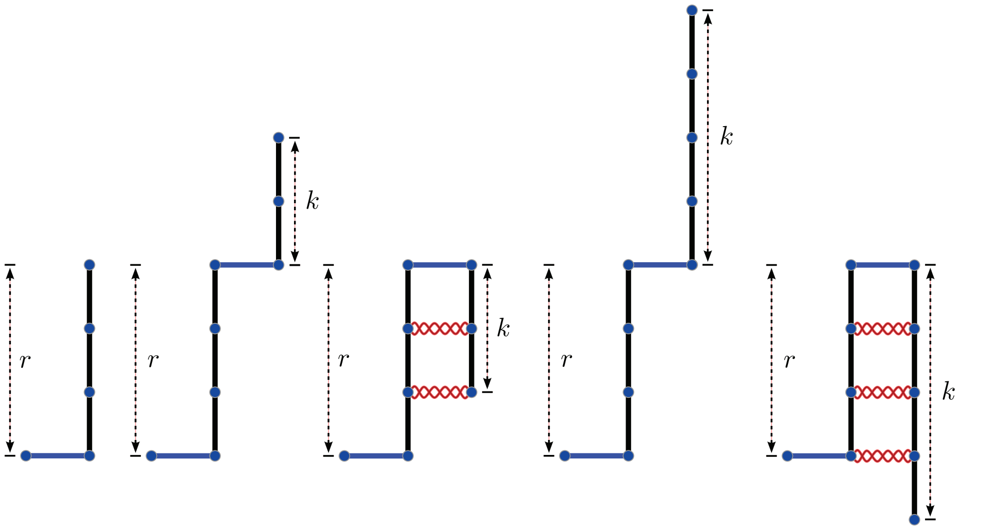
$$g_r = hz^{r+1}\left(2 + \sum_{k=0}^{r}(1+\omega^k)g_k + (1+\omega^r)\sum_{k=r+1}^{\infty} g_k\right), \qquad r \geqslant 1. \tag{3.16}$$

See figure 3. These results imply that g_r satisfies the recurrence

$$g_{r+1} - (z + \omega z)g_r + \omega^r hz^{r+2}(\omega - 1)g_r + \omega z^2 g_{r-1} = 0. \tag{3.17}$$

We have $q = \omega z$ so that (3.17) becomes

$$g_{r+1} - (z + q)g_r + q^r hz(q - z)g_r + qzg_{r-1} = 0. \tag{3.18}$$



$$2hz^{r+1} \qquad +hz^{r+1}\sum_{k=0}^{r} g_k \qquad +hz^{r+1}\sum_{k=0}^{r} \omega^k g_k \qquad +hz^{r+1}\sum_{k=r+1}^{\infty} g_k \qquad +hz^{r+1}\omega^r \sum_{k=r+1}^{\infty} g_k$$

Figure 3. Walks counted by g_r, with $r > 0$, either contain a single horizontal bond (and so are an $\rfloor$ or an $\rceil$) or can be constructed by appending an $\rfloor$ or $\rceil$ configuration of bonds to a walk counted by g_k. Summing over all these possibilities gives equation (3.16).

This can be solved with the ansatz

$$g_r = \lambda^r \sum_{m=0}^{\infty} p_m(q) q^{mr} \tag{3.19}$$

which is a solution provided that

$$\lambda^2 - \lambda(z+q) + qz = 0 \tag{3.20}$$

and

$$p_m(q) = \frac{\lambda hz(z-q)q^m}{(\lambda q^m - q)(\lambda q^m - z)} p_{m-1}(q). \tag{3.21}$$

Since $p_0(q) = 1$ this gives

$$p_m(q) = \frac{\lambda^m h^m z^m (z-q)^m q^{m(m+1)/2}}{\prod_{k=1}^m (\lambda q^k - q) \prod_{k=1}^m (\lambda q^k - z)}. \tag{3.22}$$

The quadratic equation (3.20) has the two solutions $\lambda_1 = z$ and $\lambda_2 = q = \omega z$ and the general solution for $g_r, r > 0$ is

$$g_r = A_1 g_r^{(1)} + A_2 g_r^{(2)} \tag{3.23}$$

where

$$g_r^{(i)} = \lambda_i^r + \lambda_i^r \sum_{m=1}^{\infty} \frac{\lambda_i^m h^m z^m (z-q)^m q^{m(m+1)/2}}{\prod_{k=1}^m (\lambda_i q^k - q) \prod_{k=1}^m (\lambda_i q^k - z)} q^{mr}. \tag{3.24}$$

Arguments similar to those in Brak *et al* (1992) show that $A_2 = 0$ and A_1 can be determined by noting that

$$g_0 = \tfrac{1}{2} A_1 g_0^{(1)} = hz + hz\hat{G}(z; h, 1, \omega) \tag{3.25}$$

and

$$g_1 = A_1 g_1^{(1)} = a + b\hat{G}(z; h, 1, \omega), \tag{3.26}$$

where $a = hz^2(2 + hz - \omega hz)$ and $b = hz^2(1 + hz + \omega - \omega hz)$. These simultaneous equations give

$$\hat{G}(z; h, 1, \omega) = \frac{2hzg_1^{(1)} - ag_0^{(1)}}{bg_0^{(1)} - 2hzg_1^{(1)}}, \tag{3.27}$$

which can be written as

$$\begin{aligned} 1 + \hat{G}(z; h, 1, \omega) &= \frac{2hz^2(\omega - 1)g_0^{(1)}}{bg_0^{(1)} - 2hzg_1^{(1)}} \\ &= \frac{(\omega - 1)g_0^{(1)}}{z(1 + hz + \omega - \omega hz)g_0^{(1)} - 2g_1^{(1)}}. \end{aligned} \tag{3.28}$$

The solution given by Owczarek *et al* (1993) was written as

$$1 + G(x, y, y, \omega) = \frac{1 - \omega}{2(\mathcal{H}(y, y\omega, xy(\omega - 1)) - 1) + (1 - \omega)(1 - x)}, \tag{3.29}$$

where

$$\mathcal{H}(y, q, t) = \frac{H(y, q, qt)}{H(y, q, t)} \tag{3.30}$$

and

$$H(y, q, t) = \sum_{n=0}^{\infty} \frac{q^{\binom{n}{2}}(-t)^n}{(y; q)_n (q; q)_n}. \tag{3.31}$$

The two forms can be seen to be the same when one notes that

$$\begin{aligned} 1 + \hat{G}(z; h, 1, \omega) &= 1 + G(hz, z, z, \omega) \\ &= \frac{1 - \omega}{2(\mathcal{H}(z, z\omega, hz^2(\omega - 1)) - 1) + (1 - \omega)(1 - hz)} \\ &= \frac{\omega - 1}{(1 + hz + \omega - \omega hz) - 2\mathcal{H}(z, z\omega, hz^2(\omega - 1))} \end{aligned} \tag{3.32}$$

and that

$$\mathcal{H}(z, z\omega, hz^2(\omega - 1)) = \frac{g_1^{(1)}}{zg_0^{(1)}}. \tag{3.33}$$

The implications for the singularity diagram of this expression for $\hat{G}(z; h, 1, \omega)$, and the phase transitions, will be considered in the following section.

3.4. *Solution on the special surface $z = 1/\omega$*

Before we proceed to discuss the singularity diagram let us consider the solution on the special surface defined by $q = 1$ since the solution described by (3.28) is singular when $z = 1/\omega$ though the generating function is finite for large enough ω.

The recurrence for the partial generating functions becomes

$$g_{r+1} + [hz(1 - z) - (1 + z)]g_r + zg_{r-1} = 0, \tag{3.34}$$

and now the simpler Ansatz of $g_r = C\mu^r$ can be used to find

$$1 + \hat{G}(1/\omega; h, 1, \omega) = \sqrt{\left(\frac{w^2(w - 1)}{w(w - h)^2 - (w + h)^2}\right)}. \tag{3.35}$$

When $h = 1$ we recover the previously calculated result of Brak *et al* (1992).

4. The phase diagram for a horizontal force

In order to analyse the phase transition structure we need to analyse the form of the singularity diagram as a function of the ω and h parameters. We derive a functional equation for a slight generalization of the quantity $g_r^{(1)}$. We introduce a parameter t and define the function

$$g(t;q,h,\omega) = 1 + \sum_{m=1}^{\infty} \frac{h^m \omega^{-m}\left(\frac{1}{\omega}-1\right) q^{m(m+5)/2} t^m}{\prod_{k=1}^{m}(1-q^k)(1-q^k/\omega)}. \tag{4.1}$$

Note that $g_1^{(1)}$ is equal to $zg(tq;q,h,\omega)$ evaluated at $t=1$ while $g_0^{(1)} = g(1;q,h,\omega)$.

The function $g(t;q,h,\omega)$ satisfies the functional equation

$$g(t;q,h,\omega) + g(q^2t;q,h,\omega)/\omega = (1+1/\omega+(1/\omega-1)hq^2t/\omega)g(qt;q,h,\omega). \tag{4.2}$$

Defining

$$\hat{H}(t;q,h,\omega) = g(t;q,h,\omega)/g(tq;q,h,\omega) \tag{4.3}$$

gives

$$\hat{H}(t;q,h,\omega) = (1+1/\omega+(1/\omega-1)hq^2t/\omega) - \frac{1/\omega}{\hat{H}(qt;q,h,\omega)}, \tag{4.4}$$

which leads to a continued fraction representation for $\hat{H}(t;q,h,\omega)$. Note that

$$\hat{H}(1;q,h,\omega) \equiv \hat{H}(q,h,\omega) = zg_0^{(1)}\big/g_1^{(1)} = \frac{1}{\mathcal{H}(z,z\omega,hz^2(\omega-1))} \tag{4.5}$$

and therefore

$$1+\hat{G}(z;h,1,\omega) = \frac{(\omega-1)\hat{H}(q,h,\omega)}{(1+hz+\omega-\omega hz)\hat{H}(q,h,\omega)-2}. \tag{4.6}$$

The function $\hat{H}(q,h,\omega)$ is singular on the hyperbola $q=\omega z=1$ for all values of h and the only other singularities in G come from the poles corresponding to the denominator of G being zero, i.e. determined by the solution of the equation $(1+hz+\omega-\omega hz)\hat{H}(q,h,\omega)-2=0$. This line of poles intersects the hyperbola at a point determined by solving the equation $(1+hz+\omega-\omega hz)\hat{H}(1,h,\omega)-2=0$, where $\hat{H}(1,h,\omega)$ is determined by the quadratic equation

$$\hat{H}(1,h,\omega)^2 - \left[1+\frac{1}{\omega}+\left(\frac{1}{\omega}-1\right)\frac{h}{\omega}\right]\hat{H}(1,h,\omega)+\frac{1}{\omega}=0, \tag{4.7}$$

which comes from (4.4) on setting $q=t=1$. The variables ω and h are related through the equation

$$ah^2(\omega-1) - 2\omega(\omega+1)h + \omega^3 - \omega^2 = 0 \tag{4.8}$$

which implies that the critical value of h is given by

$$h_t = \frac{(\omega+1-2\sqrt{\omega})\omega}{\omega-1}. \tag{4.9}$$

Let us consider $q_c(h,1,\omega) = z_c(h,1,\omega)\omega$. We have that $0<q_c<1$ for $1\leqslant\omega<\omega_t(h,1)$. We have argued that there is a pole in the generating function which means that there is a zero of $D=1/(1+G)$. That is, the function

$$D(q,\omega,h) \equiv \frac{[(1+hq/\omega+\omega-hq)-2\mathcal{H}(q/\omega,q,hq^2(\omega-1)/\omega^2)]}{\omega-1} \tag{4.10}$$

obeys

$$D(q_c, \omega, h) = 0. \tag{4.11}$$

We also have analyticity of $\mathcal{H}$ for $0 < q < 1$, shown by the ratio test. When $\omega = 1$ there is a simple pole in the generating function. We have

$$D(q, 1, h) \equiv \frac{1 - (1+h)q - hq^2}{1-q} \tag{4.12}$$

and so that

$$\frac{\partial D(q, 1, h)}{\partial q} < 0 \tag{4.13}$$

at $q = q_c(h, 1, 1)$. The derivative is negative for all $0 < q < 1$.

We now prove that there is a simple pole for all $1 \leqslant \omega < \omega_t(h, 1)$. For this, we compute

$$\frac{\partial D(q, \omega, h)}{\partial q} = -\frac{h}{\omega} - \frac{2}{\omega - 1}\frac{d}{dq}\mathcal{H}(q/\omega, q, hq^2(\omega-1)/\omega^2). \tag{4.14}$$

Observe that $\mathcal{H}(y, q, t)$ is related to the generating function $G_{sc}(x, y, q)$ of staircase polygons enumerated by width, height and area. Equations (4.6) and (4.9) of Prellberg and Brak (1995) imply that

$$G_{sc}(x, y, q) = y[\mathcal{H}(qy, q, qx) - 1]. \tag{4.15}$$

It follows that $\mathcal{H}(q/\omega, q, hq^2(\omega-1)/\omega^2)$ is a power series in q with non-negative coefficients. Therefore, its derivative with respect to q is positive. Hence

$$\frac{\partial D(q, \omega, h)}{\partial q} < 0 \tag{4.16}$$

and therefore there is a simple pole in the generating function at all values of $1 \leqslant \omega < \omega_t(h, 1)$.

Now, using a version of the *implicit function theorem* that gives analyticity (see chapter 6 of Krantz and Parks (2002)) it follows that $q_c(h, 1, \omega)$ is an analytic function of both ω and h.

To determine the detailed shape of the part of the phase boundary determined by the poles of $\hat{G}$ we solve the equation $(1 + hz + \omega - \omega hz)\hat{H} - 2 = 0$ numerically by evaluating H from its continued fraction expansion. That is, we write $\hat{H}$ as

$$\hat{H}(t; \omega, h, q) = (1 + 1/\omega + (1/\omega - 1)hq^2 t/\omega)(1 + \beta_0 \mathcal{C}), \tag{4.17}$$

where

$$\mathcal{C} = \cfrac{1}{1 + \cfrac{\beta_1}{1 + \cfrac{\beta_2}{1 + \cfrac{\beta_3}{\ddots}}}} \tag{4.18}$$

and

$$\beta_k = \frac{-1/\omega}{(1 + 1/\omega + (1/\omega - 1)hq^{k+2}t/\omega)(1 + 1/\omega + (1/\omega - 1)hq^{k+3}t/\omega)}. \tag{4.19}$$

To evaluate the continued fraction $\mathcal{C}$ efficiently we note that if $\mathcal{C}_m$ is the truncation of $\mathcal{C}$ at order m then $\mathcal{C}_m$ can be written as a rational function whose numerator and denominator depend on m and are determined by recurrences. This gives a convenient way to evaluate $\mathcal{C}$ to the required accuracy. In figure 4 we show the phase boundaries in the (ω, z)-plane for several values of h.

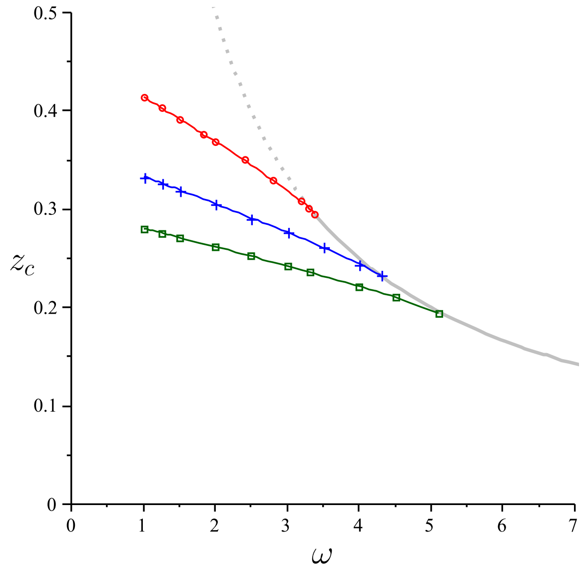


Figure 4. The radius of convergence of the generating function as a function of ω when the force is applied in the x-direction. The rectangular hyperbola is independent of the value of h. The three curves with points marked correspond to $h = 1$ (top curve), $h = 1.5$ and $h = 2.0$.

5. Extension under a fixed horizontal force

We shall now consider the average extension of the polymer as a function of the applied force at different temperatures.

From section 3 we know that $\kappa(f_x, 0, \beta)$ is a continuous function of β and f_x. Moreover for any fixed f_x the free energy $\kappa(f_x, 0, \beta)$ is analytic for $0 < \beta < \infty$ except at at most one point which we label $\beta^t(f_x)$ when it exists. This transition point is defined (see Owczarek and Prellberg 2007) via

$$\omega_t = \left(\frac{\omega_t + h}{\omega_t - h}\right)^2 \tag{5.1}$$

recalling that $h = \mathrm{e}^{\beta f_x}$. Similarly the free energy $\kappa(f_x, 0, \beta)$ is an analytic function of f_x except at the solutions of $\beta^t(f_x, 0) = \beta$. Consideration of equation (5.1) implies there is a single solution. Let the solution for this 'critical force' be labelled f_x^t and so by (5.1) it is given by the function

$$f_x^t = \frac{1}{\beta}\log\left(\frac{\mathrm{e}^{\beta/2} - 1}{\mathrm{e}^{-\beta/2} + \mathrm{e}^{-\beta}}\right), \tag{5.2}$$

which is the result (11) of Rosa *et al* (2003). In figure 5 we plot the critical force f_x^t against β^{-1}. We note that for $\beta \leqslant \beta^t(0, 0) \approx 1.218$ (equivalently $T^t \approx 0.8205$) there is no positive critical force, and that for $\beta > \beta^t(0, 0)$ there is a single critical force f_x^t.

At fixed force and below the critical temperature (which depends on the force), we have $z_c(h, 1, \omega) = 1/\omega$ and so

$$\kappa(f_x, 0, \beta) = \beta \qquad \text{for} \quad \beta \geqslant \beta^t(f_x, 0). \tag{5.3}$$

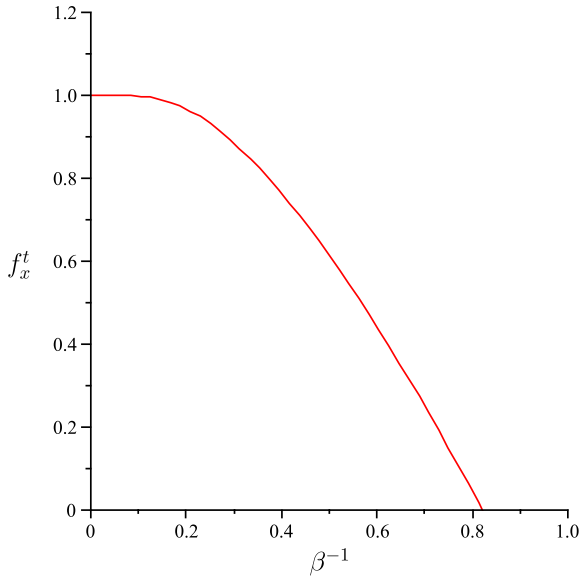


Figure 5. The temperature dependence of the critical force for horizontal pulling in the $n \to \infty$ limit. When the force is less than the critical force the walk is compact and when it is greater than the critical force it is expanded.

For $0 < \beta \leqslant \beta^t(f_x, 0)$ we know that $z_c(h, 1, \omega)$ is a strictly decreasing function of β, and so $\kappa(f_x, 0, \beta)$ is a strictly increasing function of β. Near the transition we know from Owczarek and Prellberg (2007) (see the discussion after equation (3.9)) that

$$\kappa(f_x, 0, \beta) - \beta \sim C(\beta^t - \beta)^{3/2} \qquad \text{as} \quad \beta \to (\beta^t)^- \tag{5.4}$$

and similarly

$$\kappa(f_x, 0, \beta) - \beta \sim D\big(f_x - f_x^t\big)^{3/2} \qquad \text{as} \quad f_x \to \big(f_x^t\big)^+ \tag{5.5}$$

for some constants C and D.

For $0 < \beta < \beta^t(f_x, 0)$, the singularity in z closest to the origin in $\hat{G}(z; h, 1, \omega)$ is a simple pole. From this we deduce that

$$Z_n(f_x, 0, \beta) = \mathrm{e}^{\kappa(f_x,0,\beta)n+O(1)} \qquad \text{for} \quad 0 < \beta < \beta^t(f_x, 0). \tag{5.6}$$

In the semi-continuous model (Owczarek *et al* (1993)) the following was derived for the scaling of the partition function at low temperatures

$$Z_n(f_x, 0, \beta) = \mathrm{e}^{\beta n+\kappa_s(f_x,0,\beta)n^{1/2}+O(1)} \qquad \text{for} \quad \beta^t(f_x, 0) < \beta, \tag{5.7}$$

where $\kappa_s(f_x, 0, \beta)$ is a negative non-constant analytic function of β and f_x, and also we have that $\lim_{\beta\to\beta^t} \kappa_s(f_x, 0, \beta^t) = 0$. Both the discrete model (given explicitly by Owczarek and Prellberg (2007)) and the semi-continuous model (given by Owczarek *et al* (1993)) have generating functions that have uniform asymptotics with the same algebraic structure, given by a ratio of Airy functions. In particular, the results in Owczarek *et al* (1993) depend on the scaling of the locations of the poles in the generating function which has the same scaling in both cases. Without making the explicit calculation one can surmise that equation (5.7) also holds for the discrete model.

For completeness we note that at $\beta = \beta^t(f_x, 0)$ there is an algebraic singularity in the generating function (see Owczarek and Prellberg (2007)). Assuming the conditions of Darboux's theorem hold gives us

$$Z_n(f_x, 0, \beta^t(f_x, 0)) = \mathrm{e}^{\beta^t n - \frac{2}{3}\log(n) + O(1)}. \tag{5.8}$$

One could calculate the average extension in the generalized ensemble simply by differentiating the generating function with respect to the force. In the discrete model this gives a complicated expression in terms of q-Bessel functions and its derivatives. However as the equivalence of the thermodynamic limits of the canonical ensemble and generalized ensemble is limited to $0 < \beta \leqslant \beta^t$ it is simpler to use the results above to deduce the behaviour of the average extension in the canonical ensemble directly. In the canonical ensemble the average extension $\langle s_x \rangle_n(f_x, f_y, \beta)$ is defined by

$$\langle s_x \rangle_n(f_x, f_y, \beta) = \frac{1}{\beta}\frac{\partial \log Z_n(f_x, f_y, \beta)}{\partial f_x}. \tag{5.9}$$

Assuming the conditions for differentiating the asymptotic expansion term-by-term hold the result (5.6) implies that

$$\langle s_x \rangle_n(f_x, 0, \beta) = \frac{1}{\beta}\frac{\partial \kappa(f_x, 0, \beta)}{\partial f_x} n + O(1) \qquad \text{for} \quad 0 < \beta < \beta^t, \tag{5.10}$$

so that the thermodynamic limit extension per unit length

$$S_x(f_x, f_y, \beta) = \lim_{n\to\infty} \frac{\langle s_x \rangle_n(f_x, f_y, \beta)}{n} \tag{5.11}$$

is

$$S_x(f_x, 0, \beta) = \frac{1}{\beta}\frac{\partial \kappa(f_x, 0, \beta)}{\partial f_x} > 0 \qquad \text{for} \quad 0 < \beta < \beta^t. \tag{5.12}$$

Moreover the scaling near β^t in equation (5.5) as given by Owczarek and Prellberg (2007) implies that

$$S_x(f_x, 0, \beta) \to 0^+ \qquad \text{as} \quad \beta \to (\beta^t)^-. \tag{5.13}$$

One can calculate this quantity from the generalized ensemble in the semi-continuous model (see equation (3.46) in Owczarek *et al* 1993) and analyse it in a more straightforward manner than in the discrete case (since it involve Bessel functions rather than q-Bessel functions), and it shows the same behaviour.

On the other hand, the result (5.7) (once again assuming differentiability of the asymptotic expansion) implies that

$$\langle s_x \rangle_n(f_x, 0, \beta) = \frac{1}{\beta}\frac{\partial \kappa_s(f_x, 0, \beta)}{\partial f_x} n^{1/2} + O(1) \qquad \text{for} \quad \beta^t < \beta \tag{5.14}$$

and so that

$$S_x(f_x, 0, \beta) = 0 \qquad \text{for} \quad \beta^t < \beta. \tag{5.15}$$

We have calculated the stress–strain curves by computing the free energy from the boundary of convergence (section 4) and then numerically differentiating. Using these results and the above arguments we can make the following comments. In all cases the function of the average extension per unit length $S_x(f_x, 0, \beta)$ is a continuous function of f_x for $f_x \geqslant 0$.

At high temperatures where $\beta < \beta^t(0, 0)$ there is no critical force and the average extension per unit length $S_x(0, 0, \beta) > 0$ at zero force. At such fixed β the function $S_x(f_x, 0, \beta)$ is an analytic function of f_x for $f_x \geqslant 0$ and is strictly increasing with increasing force. There is a unit horizontal asymptote, approached from below for large forces. There

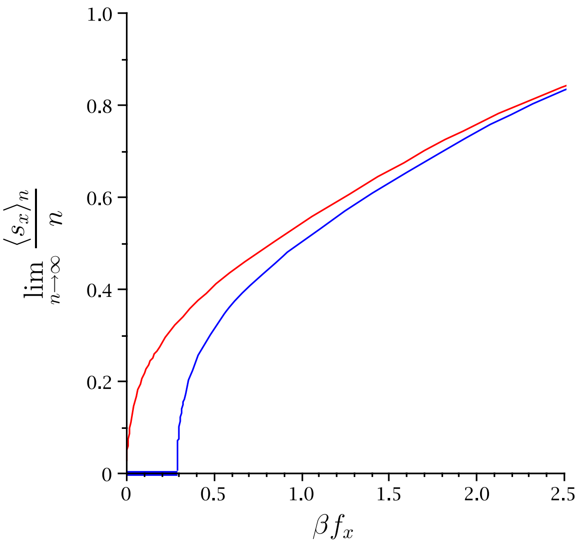


Figure 6. The dependence of $\lim_{n\to\infty} \langle s_x \rangle_n / n$, the limiting average horizontal span per unit length, on βf_x for different temperatures: at $\beta = \beta_c$ (upper curve) and at $\beta = \log 4 > \beta_c$ (lower curve). Note that above the critical temperature the behaviour is qualitatively the same as that shown in figure 2.

is a finite nonzero slope $\frac{\partial S_x(f_x,0,\beta)}{\partial f_x}$ at $f_x = 0$. The qualitative behaviour is the same as that shown in figure 2 for the $\omega = 1$ case.

At the critical temperature for zero force $\beta = \beta^t(0, 0)$ the average extension per unit length $S_x(0, 0, \beta) = 0$ at zero force. Again the function $S_x(f_x, 0, \beta^t(0, 0))$ is an analytic function of f_x for $f_x > 0$, is strictly increasing with increasing force, and has a unit horizontal asymptote, approached from below for large forces. Now however the slope $\frac{\partial S_x(f_x,0,\beta^t(0,0))}{\partial f_x}$ diverges when $f_x \to 0^+$ as $f_x^{-1/2}$. This is shown in figure 6.

At low temperatures where $\beta > \beta^t(0, 0)$ (so there is a critical force $f_x^t > 0$) there are two regimes. For $0 \leqslant f_x \leqslant f_x^t$ the average extension per unit length $S_x(f_x, 0, \beta) = 0$ regardless of the force. However for $f_x^t < f_x$ the function $S_x(f_x, 0, \beta)$ is an analytic function of f_x, is strictly increasing with increasing force, and has a unit horizontal asymptote, approached from below for large forces. Again the slope $\frac{\partial S_x(f_x,0,\beta)}{\partial f_x}$ diverges when $f_x \to \left(f_x^t\right)^+$ as $\left(f_x - f_x^t\right)^{-1/2}$. This is illustrated in figure 6.

6. The full model: pulling in both directions

6.1. *No self-interactions* ($\omega = 1$)

As in subsection 3.1 which describes the solution when there is no vertical pulling (and no self-interactions) one can write down a simple functional equation for the generating function $G(x, y_+, y_-, 1)$ as

$$G(x, y_+, y_-, 1) = x\left(1 + \frac{y_+}{1 - y_+} + \frac{y_-}{1 - y_-}\right)(1 + G(x, y_+, y_-, 1)) \tag{6.1}$$

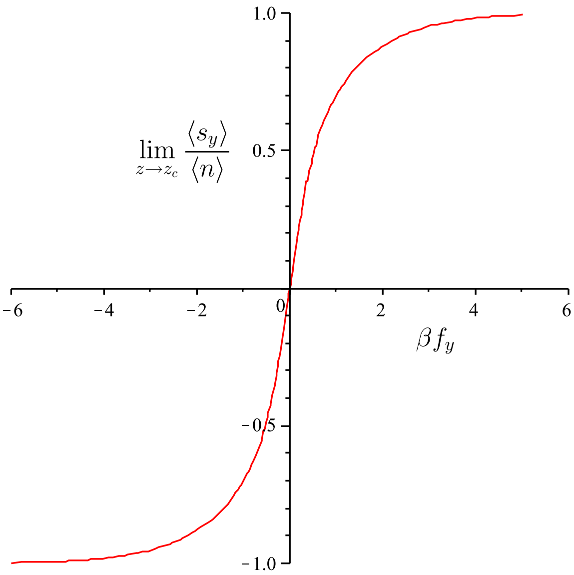


Figure 7. A plot of $\lim_{z\to z_c} \langle s_y\rangle/\langle n\rangle$ when $\omega = 1$ against βf_y.

so that

$$1 + G(x, y_+, y_-, 1) = \frac{1}{1 - x\frac{1-y_+y_-}{(1-y_+)(1-y_-)}}, \tag{6.2}$$

and setting $x = hz$, $y_+ = zv$ and $y_- = z/v$ we get

$$1 + \hat{G}(z; h, v, 1) = \frac{1}{1 - hz\left[\frac{1-z^2}{1-(v+v^{-1})z+z^2}\right]}. \tag{6.3}$$

So the answer is a simple rational function, and the critical z (that is $z_c(h, v, 1)$) is the root of a cubic. For $h = v = 1$ this simplifies as expected.

If we set $f_x = 0$ then

$$1 + \hat{G}(z; 1, v, 1) = \frac{1}{1 - z\left[\frac{1-z^2}{1-(v+v^{-1})z+z^2}\right]}, \tag{6.4}$$

and from this we can readily calculate the ratio $\langle s_y\rangle/\langle n\rangle$ and take the thermodynamic limit by letting $z \to z_c(1, v, 1)$. In figure 7 is a plot of $\lim_{z\to z_c}\langle s_y\rangle/\langle n\rangle$ against βf_y.

6.2. Solution of the full model

In the appendix of Owczarek *et al* (1993) it was shown that if one adds fugacity variables y_+ for steps in the positive vertical direction and y_- for steps in the negative vertical direction then a generalization of the method for solving the standard problem yields the generating function $G(x, y_+, y_-, \omega)$ as described in section 2. Using $q_+ = y_+\omega$ and $q_- = y_-\omega$ it is given by

$$1 + G(x, y_+, y_-, \omega) = \frac{(1-\omega)}{[2\bar{\mathcal{H}}(x, y_+, y_-, \omega) - (1 + \omega + (1-\omega)x)]}, \tag{6.5}$$

where

$$\bar{\mathcal{H}}(x, y_+, y_-, \omega) = \frac{\left(A_0^+ + B_0^+\right)\left(A_1^+ - B_1^+\right) - \left(A_0^- + B_0^-\right)\left(A_1^- - B_1^-\right)}{\left(A_0^+ + B_0^+\right)\left(A_0^+ - B_0^+\right) - \left(A_0^- + B_0^-\right)\left(A_0^- - B_0^-\right)}, \tag{6.6}$$

with

$$A_r^{\pm} = \sum_{m=0}^{\infty} \frac{x^{2m}(\omega-1)^{2m}(q_+q_-)^{m(m+r)}{q_\pm}^m}{\prod_{k=1}^m P[(q_+q_-)^{k-1}q_\pm]P[(q_+q_-)^k]}, \tag{6.7}$$

$$B_r^{\pm} = \sum_{m=0}^{\infty} \frac{x^{2m+1}(\omega-1)^{2m+1}(q_+q_-)^{m(m+r)}{q_\pm}^{r+m+1}}{P[(q_+q_-)^m q_\pm]\prod_{k=1}^m P[(q_+q_-)^{k-1}q_\pm]P[(q_+q_-)^k]} \tag{6.8}$$

and

$$P[\lambda] = (\lambda - 1)(\lambda - \omega). \tag{6.9}$$

Note that $q_+q_- = q^2$, and given that all the parameters are positive we have $q = \sqrt{q_+q_-}$. This solution is then a clear generalization of the form for the horizontal pulling model where

$$1 + G(x, y, y, \omega) = \frac{1-\omega}{[2\mathcal{H}(y, y\omega, xy(\omega-1)) - (1 + \omega + (1-\omega)x)]}, \tag{6.10}$$

where $\mathcal{H}(y, q, t) = H(y, q, qt)/H(y, q, t)$ is given in terms of $H(y, q, t)$ defined by equation (3.31).

However the problem of generalizing the analysis of Prellberg (1995) is a daunting one. On the other hand we can still make some deductions about the behaviour of the generating function. Since the partition function is positive we know that $\hat{G}(z; h, v, \omega)$ is a strictly increasing function of z for fixed $h, v, \omega > 0$.

Let us consider $\omega \geqslant 1$. The functions $A_r^{\pm}$ and $B_r^{\pm}$ converge whenever $q < 1$ and moreover there are singularities when $|q| = 1$. The solution for the generating function $G(x, y_+, y_-, \omega)$ is given in the following section and one finds that $G(x, y_+, y_-, \omega)$ on this surface is finite when $\omega > \omega_t$, where ω_t is given by the solution of equation (6.27). The only singularities that can occur in the generating function for $q < 1$ are poles occurring when the denominator of (6.5) is zero. The nature of these poles is unclear but we conjecture that they are simple poles and that they only exist when $\omega < \omega_t$.

6.3. Solving the full model on the special surface $z = 1/\omega$

While expression (6.6) is rather unwieldy, it is possible to find a sub-manifold of parameters for which the solution can be made more explicit. If we restrict to

$$q_+q_- = q^2 = 1 \qquad \text{that is} \quad q = \omega z = 1, \tag{6.11}$$

then (6.6) has a singular limit. This is analogous to the fact that in the case of (6.10) one obtains an algebraic function for $q = 1$.

Hence we have $q_+ = v$ and $q_- = 1/v$. Also, we shall retain the variable x for convenience during the calculations before substituting $x = h/\omega$ as required in the final expressions.

Let $g_r^{\pm} = {y_\pm}^{-r}G_r^{\pm}$ where $G_r^{\pm}$ is the generating function for walks with r steps in the positive and negative directions respectively, and we have in analogy with the derivation of the full problem

$$\begin{aligned} g_{r+4}^{\pm} &- (\omega+1)(q_\pm+1)g_{r+3}^{\pm} + (\omega(1+{q_\pm}^2) + (\omega+1)^2 q_\pm)g_{r+2}^{\pm} \\ &- \omega q_\pm(\omega+1)(q_\pm+1)g_{r+1}^{\pm} + \omega^2{q_\pm}^2 g_r^{\pm} = q_\pm x^2(\omega-1)^2 g_{r+2}^{\pm}. \end{aligned} \tag{6.12}$$

The characteristic polynomial is

$$P_{\pm}(\lambda) = (\lambda - 1)(\lambda - \omega)(\lambda - q_{\pm})(\lambda - q_{\pm}\omega) - q_{\pm}x^2(\omega - 1)^2\lambda^2. \tag{6.13}$$

Despite being a polynomial of degree four, $P_{\pm}(\lambda)$ has sufficient symmetry to allow for simple explicit solutions. The key observation is that if λ is a root of $P_{\pm}(\lambda)$, then so is $q_{\pm}\omega/\lambda$. If we define

$$\mu_{\pm} = \lambda + \frac{\omega q_{\pm}}{\lambda}, \tag{6.14}$$

then $\mu_{\pm}$ satisfies

$$\mu_{\pm}^2 - (\omega + 1)(q_{\pm} + 1)\mu_{\pm} + (\omega + q_{\pm})(1 + \omega q_{\pm}) - x^2(\omega - 1)^2 = 0. \tag{6.15}$$

We can therefore obtain all four roots of $P_{\pm}(\lambda)$ by solving the quadratic equation (6.15) for $\mu_{\pm}$, followed by solving the quadratic equation (6.14) for λ.

The general solution for (6.12) is a linear combination

$$g_r^{\pm} = \sum_{i=1}^{4} A_i \lambda_{\pm,i}^r \qquad \text{respectively} \qquad G_r^{\pm} = y_{\pm}{}^r \sum_{i=1}^{4} A_i \lambda_i^r. \tag{6.16}$$

After some algebra the generating function $1 + \hat{G}(1/\omega; h, v, \omega) = G(h/\omega, v/\omega, 1/v\omega, \omega)$ can be found to be

$$1 + \hat{G}(1/\omega; h, v, \omega) = \frac{(t_1t_2\omega - 1)(t_1v - 1)(t_2v - 1)(\omega - 1)\omega^2}{D(t_1, t_2)}, \tag{6.17}$$

where

$$\begin{aligned} D(t_1, t_2) = {} & t_1t_2(\omega - 1)^2h^2 + (\omega - 1)(t_1t_2v - 1)(t_1t_2\omega v - 1)h\omega \\ & - (t_1 - 1)(t_1v - 1)(t_2 - 1)(t_2v - 1)\omega^3 \end{aligned} \tag{6.18}$$

with t_1 and t_2 the two distinct roots of $L(t) = 0$ with

$$L(t) = vh^2(\omega - 1)^2t^2 - (t - 1)(\omega t - 1)(vt - 1)(\omega vt - 1)\omega^2. \tag{6.19}$$

We note that $L(t)$ is a quartic polynomial in t. If we let

$$s = \frac{1}{t} + v\omega t \tag{6.20}$$

then s satisfies

$$s^2 - (\omega + 1)(v + 1)s + (\omega + v)(1 + \omega v) = vh^2\frac{(\omega - 1)^2}{\omega^2}, \tag{6.21}$$

and the two solutions of this equation are

$$s_{\pm} = \frac{(\omega + 1)(v + 1) \pm \sqrt{(\omega - 1)^2(v^2 - 2v + 1 + 4vh^2/\omega^2)}}{2}. \tag{6.22}$$

Now only one of the solutions of (6.20) is applicable, namely

$$t = \frac{s - \sqrt{s^2 - 4v\omega}}{2v\omega} \tag{6.23}$$

which gives us that

$$t_1 = \frac{s_+ - \sqrt{s_+^2 - 4v\omega}}{2v\omega} \tag{6.24}$$

and

$$t_2 = \frac{s_- - \sqrt{s_-^2 - 4v\omega}}{2v\omega}. \tag{6.25}$$

Importantly, on substitution into the generating function the denominator can be found to be a polynomial with a factor

$$(v\omega^2 + 2h\omega v + vh^2 - 2vh^2\omega + \omega^4 v - 2h\omega^3 v + vh^2\omega^2 - \omega^3 - v^2\omega^3) \quad (6.26)$$

and no other relevant factors. Hence the generating function is singular on the curve $q = 1$ when this factor is zero. It can be seen that the algebraic singularity (a square root) occurs in the generating function at the same place by considering the discriminant of (6.13). It can therefore be deduced that the exponent $\gamma_u = 1/2$ describing the singularity in the generating function approaching the transition point tangentially (as described in Owczarek *et al* 1993). The exponent is independent of the values of h and v and so of whether there is a horizontal and/or vertical pulling force.

We therefore have the location of the critical point as

$$\omega^2(1+\omega^2) + 2\omega(1-\omega^2)h + (1-\omega)^2h^2 = \omega^3(v + 1/v). \quad (6.27)$$

One can rewrite this as

$$\cosh(\beta f_y/2) = \exp(-\beta/2)\cosh(\beta) - \exp(-\beta)\sinh(\beta/2)(\exp(\beta f_x) - 1). \quad (6.28)$$

When there is no horizontal force, that is, $h = 1$, we therefore find the critical point to be when

$$(\omega^2+1)^2 = \left(v + 2 + \frac{1}{v}\right)\omega^3, \quad (6.29)$$

which reduces to the known result of Binder *et al* (1990) when $v = 1$. From this equation the critical force temperature plot can be found as

$$f_y^t = \beta^{-1}\cosh^{-1}(2\mathrm{e}^{-\beta}\cosh^2(\beta) - 1). \quad (6.30)$$

In figure 8 we plot the critical force against temperature for vertical pulling. Note that as the temperature approaches the critical value for no pulling force the slope of this curve diverges in contrast to the analogous horizontal pulling curve.

Note that when $v = 1$ in (6.27) we find equation (5.1) that was derived in a previous section.

7. Functional equation method

7.1. Horizontal pulling

For the case of horizontal pulling we can construct a recursive functional equation for the partial generating function, cf section 2. Let us define

$$g_r(x, y, \omega) = \begin{cases} 2G_r(x, y, y, \omega) & \text{if} \quad r \geqslant 1 \\ G_0(x, y, y, \omega) & \text{if} \quad r = 0 \end{cases} \quad (7.1)$$

so that

$$F(p) = \sum_{r\geqslant 0} g_r p^r. \quad (7.2)$$

The functional equation is constructed by considering what happens when an extra column is added to the left of a walk. Let $\mathcal{P}_r$ be the set of all paths with at least one horizontal step

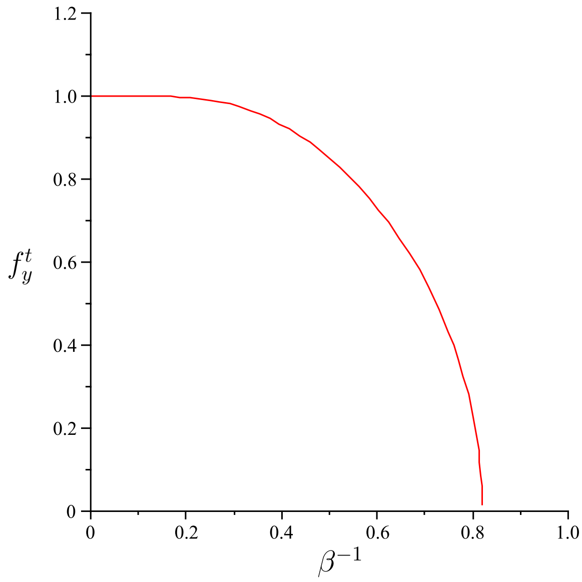


Figure 8. The temperature dependence of the critical force for vertical pulling in the $n \to \infty$ limit.

followed by $r \geqslant 0$ first column vertical steps. Let r' be the number of second column vertical steps. We can partition $\mathcal{P}_r$ into the following five disjoint subsets.

Case I. The walk has only one step. This is generated by x.

Case II. These are all walks with only one horizontal step and at least one first column vertical step. These are generated by $2xyp/(1-yp)$, the factor of two giving all upwards and all downwards sequences of steps, both generated by $yp/(1-yp)$.

Case III. These are all paths with at least two horizontal steps and the first column vertical steps (if any) are in the *same* direction to the second column vertical steps (if any). These are generated by $xF(1)/(1-yp)$. There is no factor of two for the following reason. The product $xF(1)/(1-yp)$ corresponds to concatenating a sequence of vertical steps, $V \to 1/(1-yp)$ to an arbitrary path $F(1)$. The generating variable p is set to one in $F(p)$ since the leftmost vertical steps arise from the V sequence. If the first vertical sequence of steps of $F(1)$ are upwards, then the V steps are interpreted as also being upwards (and hence no contacts are created by the concatenation, thus no ω factor). If the first vertical sequence of steps of $F(1)$ are downwards, then the V steps are interpreted as also being downwards (and again, no contacts are created by the concatenation).

Case IV. These are all paths with at least two horizontal steps and $0 < r \leqslant r'$ and with the further condition that the vertical steps in the first column are in the *opposite* direction to those in the second column. These are generated by $xypF(\omega yp)/(1-yp)$. The argument for this form is similar to that of Case III, except now contacts are created by the concatenation. The contacts are accounted for as follows. All new contacts occur in the overlap between the first and second columns. Since the p in $F(p)$ tracks the number of vertical steps in the second column, the new contacts can be accounted for by replacing p by ωp. The factor of yp in $F(\omega yp)$ is interpreted as giving rise to first r' vertical steps in the *first* column (these

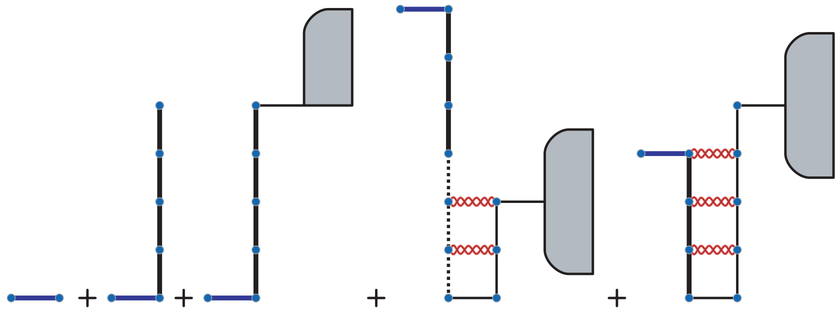


Figure 9. Schematic representation of the terms of the functional equation (7.3) arising from the five cases described in section 7.1.

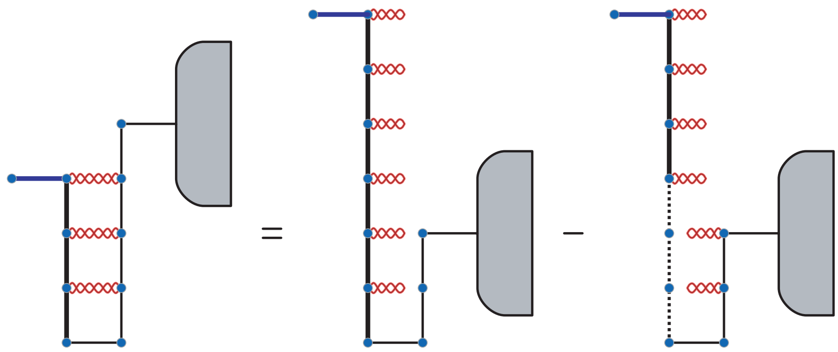


Figure 10. Schematic representation of contribution of Case V to the functional equation.

can be thought of as 'virtual steps') and the remaining $r' - r$ vertical steps are generated by $1/(1 - yp)$ and are interpreted as being concatenated on to the virtual steps, as illustrated by the fourth term in figure 9.

Case V. These are all paths with at least two horizontal steps and $0 < r' \leqslant r$ and with the further condition that vertical steps in the first column are in the *opposite* direction to those in the second column. These are generated by $x\omega yp[F(1) - F(\omega yp)]/(1 - \omega yp)$ which can be shown using inclusion–exclusion. The term $x\omega yp/(1 - \omega yp)$ counts an infinite sequence of vertical bonds and contacts. So the generating function, $T_1 = x\omega yp F(1)/(1 - \omega yp)$, counts all the required configurations, but also those with $r' > r$. The contribution of these over-counted configurations is then given by $T_2 = x\omega yp F(\omega yp)/(1 - \omega yp)$. Hence the contribution of this case is $T_1 - T_2$. See figure 10.

Combining all five cases together, as illustrated in figure 9, generates all the walks. Thus we get

$$F(p) = x + 2x\frac{yp}{1 - yp} + x\frac{1}{1 - yp}F(1) + x\frac{yp}{1 - yp}F(\omega yp) + x\frac{\omega yp}{1 - \omega yp}[F(1) - F(\omega yp)]. \tag{7.3}$$

This functional equation can be solved for $F(p)$ by the method of iteration (Bousquet-Mélou 1996).

The case $\omega y = 1$ is much simpler to solve. Letting $\omega y = 1$ gives

$$F(p) = x + 2x\frac{yp}{1-yp} + x\frac{1}{1-yp}F(1) + x\frac{yp}{1-yp}F(p) + x\frac{p}{1-p}[F(1) - F(p)]. \tag{7.4}$$

Note, to find $F(1)$ from equation (7.4) we cannot put $p = 1$ because of the denominator $1 - p$. To avoid this problem, first collect coefficients of $F(p)$ to give

$$K(p)F(p) = x(1-p)(1+yp) + x(1-yp^2)F(1) \tag{7.5}$$

where the 'kernel', $K(p)$, is given by

$$K(p) = yp^2 - (1 - x + y + xy)p + 1. \tag{7.6}$$

If we can put $K(p) = 0$ in (7.5) then, since the left-hand side is zero, we can solve for $F(1)$. Note, the condition $K(p) = 0$ implicitly constrains p, which, since $K(p)$ is quadratic in p, implies that we get two possible functions $p_\pm(x, y)$. However some care must be taken as this way of finding $F(p)$ assumes $F(p)K(p) = 0$ which is only the case if $\lim_{p\to p_\pm} F(p)K(p) = 0$. Thus, we first assume this is the case for one of the solutions, say p_+ and then verify this assumption once $F(p)$ has been explicitly computed. As is readily shown, each of the two assumptions $\lim_{p\to p_+} F(p)K(p) = 0$ and $\lim_{p\to p_-} F(p)K(p) = 0$ gives rise to *different* functions, denoted $F_\pm(p)$. In fact, $F(p)$ is an algebraic function and each of the two functions $F_\pm(p)$ is the two branches of $F(p)$. The limit $\lim_{p\to p_+} F(p)K(p)$ only vanishes if the correct branch is combined with the correct limit (the other branch has a pole at p_+ and hence the limit is the non-zero residue of $F(p)$ at p_+).

Thus, assuming $\lim_{p\to p_+} F_+(p)K(p) = 0$ and taking the limit as $p \to p_+$ on both sides of (7.5) gives $F_+(1)$. Thus we obtain the branch $F_+(1)$ on the line $\omega y = 1$ as

$$F_+(1) = -\frac{(1-p_+)(1+p_+y)}{1-p_+^2 y} \tag{7.7}$$

or, explicitly

$$1 + F_+(1) = \sqrt{\frac{y-1}{x^2(y-1) + 2x(y+1) + y - 1}}. \tag{7.8}$$

Using this solution, one then verifies the assumption that $\lim_{p\to p_+} F_+(p)K(p) = 0$. This solution has a square root singularity at

$$x^2(y-1) + 2x(y+1) + y - 1 = 0, \tag{7.9}$$

which gives the same critical value of x, x_c as given by equation (5.1) using the transformations $x = h/\omega$ and $y = 1/\omega$. Thus we see that, using this method, x_c arises via p_+ and hence from the kernel.

The functional equation (7.3) is also closely linked to the recurrence relation (3.16). If we make the substitution (2.21) into (7.3) and equate coefficients of p, then, for $r > 0$ we get

$$g_r = xy^{r+1}\left(2 + \sum_{k\geqslant 0} g_k + \sum_{k=0}^{r-1}\omega^k g_k + \omega^r \sum_{\kappa\geqslant 0} g_k - \omega^r \sum_{k=0}^{r-1} g_k\right) \tag{7.10}$$

which is readily put in the same form as (3.16).

7.2. Vertical pulling

Let us define

$$\hat{F}^+(p) = \sum_{r=0}^{\infty} G_r^+(x, vy, y/v, \omega)p^r \tag{7.11}$$

and

$$\hat{F}^{-}(p) = \sum_{r=1}^{\infty} G_r^{-}(x, y/\bar{v}, y\bar{v}, \omega) p^r. \tag{7.12}$$

Using similar arguments to the derivation of equation (7.3) we obtain the following pair of coupled equations.

$$\begin{aligned}\hat{F}^{+}(p) = {} & x + xv\frac{ypv}{1-ypv} + x\frac{1}{1-yp}\hat{F}^{+}(1) + x\frac{ypv}{1-ypv}\hat{F}^{-}(\omega ypv)\\ & + x\frac{\omega ypv}{1-yp\omega v}[\hat{F}^{-}(1) - \hat{F}^{-}(\omega ypv)]\end{aligned} \tag{7.13}$$

and

$$\begin{aligned}\hat{F}^{-}(p) = {} & x\frac{yp\bar{v}}{1-yp\bar{v}} + x\frac{1}{1-yp\bar{v}}\hat{F}^{-}(1) + x\frac{yp\bar{v}}{1-yp\bar{v}}\hat{F}^{+}(\omega yp\bar{v})\\ & + x\frac{\omega yp\bar{v}}{1-\omega yp\bar{v}}[\hat{F}^{+}(1) - \hat{F}^{+}(\omega yp\bar{v})].\end{aligned} \tag{7.14}$$

These equations can again be solved by the method of iteration, resulting in complex q-series similar to (6.6).

There is also the simple case occurring when $\omega y = 1$. Using the notation

$$L'(a) = \frac{1}{1-a}, \qquad L(a) = aL'(a) \qquad \text{and} \qquad \Delta L(a) = L(ya) - L(a),$$

we can write the two functional equations as

$$\overline{F}^{+}(p) = 1 + L(ypv) + L'(ypv)\overline{F}^{+}(1) + L(ypv)\overline{F}^{-}(pv) + L(pv)[\overline{F}^{-}(1) - \overline{F}^{-}(pv)] \tag{7.15}$$

and

$$\overline{F}^{-}(p) = L(yp\bar{v}) + L'(yp\bar{v})\overline{F}^{-}(1) + L(yp\bar{v})\overline{F}^{+}(p\bar{v}) + L(pv)[\overline{F}^{+}(1) - \overline{F}^{+}(p\bar{v})], \tag{7.16}$$

where

$$x\overline{F}^{+} = \hat{F}^{+}|_{\omega y=1} \qquad \text{and} \qquad x\overline{F}^{-} = \hat{F}^{-}|_{\omega y=1}.$$

Solving the two equations for $\overline{F}^{+}(p)$ and $\overline{F}^{-}(p)$ gives the pair

$$\begin{aligned}K^{+}(p,v)\overline{F}^{+}(p) = {} & 1 + L(ypv) + xL(yp)\Delta L(pv) + [L'(ypv) + xL(p)\Delta L(pv)]\overline{F}^{+}(1)\\ & + [L(pv) + xL'(yp)\Delta L(pv)]\overline{F}^{-}(1)\end{aligned} \tag{7.17}$$

and

$$\begin{aligned}K^{-}(p,v)\overline{F}^{-}(s) = {} & L(yp\bar{v}) + xL(yp)\Delta L(p\bar{v})[1 + L(yp)]\\ & + [L'(yp\bar{v}) + xL(p)\Delta L(p\bar{v})]\overline{F}^{-}(1)\\ & + [L(p\bar{v}) + xL'(yp)\Delta L(p\bar{v})]\overline{F}^{+}(1),\end{aligned} \tag{7.18}$$

where the two kernels are given by

$$K^{+}(p,v) = (1-p)(1-yp)(1-pv)(1-ypv) - x^2p^2v(y-1)^2 \tag{7.19}$$

$$K^{-}(p,v) = K^{+}(p,\bar{v}). \tag{7.20}$$

Thus we choose p such that

$$K^{-}(p(v), v) = K^{+}(p(\bar{v}), \bar{v}) = 0, \tag{7.21}$$

which is the same equation as the characteristic equation (6.13) with $p \to \lambda$ and y replaced by $1/\omega$. Thus we see that the kernel that arises from the functional equation approach corresponds to the characteristic equation (6.13) required to solve the Temperley recurrence relations (6.12).

8. Three-dimensional model

The model can be generalized to a three-dimensional partially directed walk model in which the walk is self-avoiding, can take steps in the $+x$- or $+y$-directions or in the $\pm z$-directions. Again it will be convenient to require that the first step is in the $+x$- or $+y$-direction. We shall only consider a force applied in the (x, y)-plane and as such we shall keep track of the span in the x- and y-directions as well as the number of contacts.

If we write c_n for the number of these walks with n steps it is easy to see that

$$\lim_{n\to\infty} n^{-1} \log c_n = \log[(3+\sqrt{17})/2]. \tag{8.1}$$

Suppose that $c_n(s_x, s_y, m)$ is the number of walks with n steps, m contacts, and with spans s_x and s_y in the x- and y-directions. The corresponding canonical partition function is

$$Z_n(h_x, h_y, \omega) = \sum_{s_x, s_y, m} c_n(s_x, s_y, m) h_x^{s_x} h_y^{s_y} \omega^m \tag{8.2}$$

and we define the generating function

$$\hat{G}(z; h_x, h_y, \omega) = \sum_n Z_n(h_x, h_y, \omega) z^n. \tag{8.3}$$

Concatenation arguments can be used, as in section 3, to establish the existence of the limiting free energy

$$\kappa(h_x, h_y, \omega) = \lim_{n\to\infty} n^{-1} \log Z_n(h_x, h_y, \omega). \tag{8.4}$$

Methods exactly analogous to those in section 3 can be used to show that $\kappa(h_x, h_y, \omega)$ is convex and continuous, and differentiable almost everywhere. At fixed ω, h_x and $h_y G$ converges if $z < z_c(h_x, h_y, \omega) = \exp[-\kappa(h_x, h_y, \omega)]$, and the phase boundary $z = z_c$ is continuous.

If we turn off the interactions by setting $\omega = 1$ and write $G_0 \equiv G(z; h_x, h_y, 1)$ then G_0 satisfies the equation

$$G_0 = (h_x + h_y)(G_0 + 1)z + \frac{2z^2(h_x + h_y)}{1 - z}(G_0 + 1) \tag{8.5}$$

so that

$$1 + G_0 = \frac{1 - z}{1 - z - z(z+1)(h_x + h_y)}. \tag{8.6}$$

The force–extension curve can be calculated as in section 3 and this has the same general form as for the two-dimensional model, and as found experimentally for good solvent conditions (Gunari *et al* 2007).

For attractive interactions ($\omega > 1$) the Temperley approach described in section 3 for the two-dimensional case immediately generalizes to this model. Defining partial generating functions as in section 2, the partial generating functions obey the relations

$$g_0 = (h_x + h_y)z(1 + G) \tag{8.7}$$

and

$$g_r = (h_x + h_y)z^{r+1}\left(2 + \sum_{k=0}^{r}(1 + \omega^k)g_k + (1 + \omega^r)\sum_{k>r} g_k\right), \tag{8.8}$$

so that g_r satisfies the relation

$$g_{r+1} - (z + q)g_r + q^r(h_x + h_y)z(q - z)g_r + qzg_{r-1} = 0 \tag{8.9}$$

with $q = \omega z$.

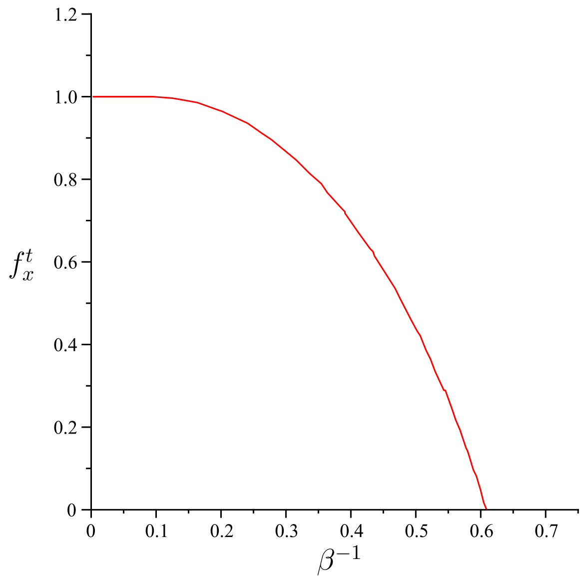


Figure 11. The temperature dependence of the critical force for the three-dimensional model in the $n \to \infty$ limit when the force is applied in the *x*-direction.

The analysis goes through as in section 3 and one can find the temperature dependence of the critical force. By choosing the relative magnitudes of h_x and h_y one can change the direction in the (x, y)-plane in which the force is applied. In all cases the force–temperature curve is monotonic and does not show reentrance. Presumably this is because the model does not have extensive ground state entropy. The phase diagram can also be calculated, using the same methods as in section 3, with qualitatively similar results.

If we set $h_y = 0$ we reproduce the results of section 3. We consider two other cases. First we set $h_x = h$ and $h_y = 1$. This corresponds to applying a force in the *x*-direction. We show the critical force–temperature curve in figure 11 and the boundary of convergence in figure 12.

These are qualitatively similar to the corresponding figures for horizontal pulling in two dimensions, though with quantitative differences, of course. In particular, the critical force–temperature curve has zero slope in the $T \to 0$ limit and is monotone decreasing. We also set $h_x = h_y = h$ which corresponds to pulling in the xy-plane but at 45° to the *x*-axis. We show the critical force–temperature curve in figure 13 and the boundary of convergence in figure 14.

The critical force now has negative limiting slope in the $T \to 0$ limit but remains monotone decreasing. This is because of the curious feature of this model that the ground state has no (extensive) entropy in the compact state but acquires entropy under the influence of a force. The low temperature behaviour can be understood by the following crude low temperature argument. Think of an *n*-edge walk at low temperature *T* under a tensile force f at 45° to the *x*-axis. If $n - m$ edges of the walk are in a compact state and the remaining m edges are extended the (extensive) free energy can be written as

$$F = (n - m)\epsilon - fm - Tm \log 2, \tag{8.10}$$

where $\epsilon < 0$ is the vertex–vertex attractive energy. Differentiating with respect to m and setting the derivative equal to zero gives

$$f = -\epsilon - T \log 2. \tag{8.11}$$

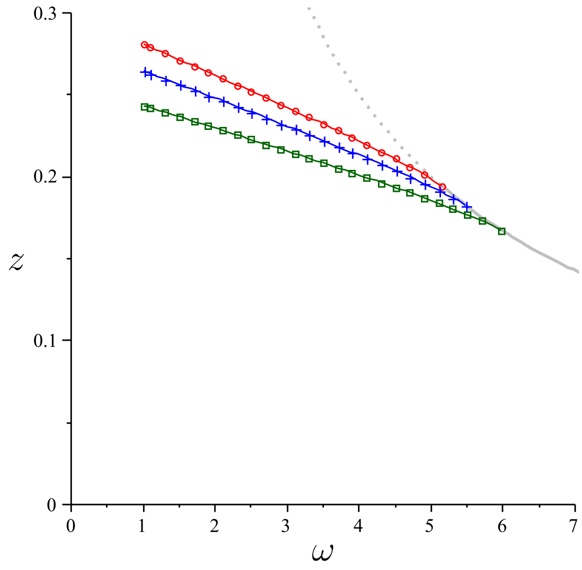


Figure 12. The boundary of convergence of the generating function as a function of ω for the three-dimensional model when the force is applied in the x-direction. The rectangular hyperbola is independent of the value of h_x. The three curves with points marked correspond to $h_x = 1$ (top curve), $h_x = 1.2$ and $h_x = 1.5$.

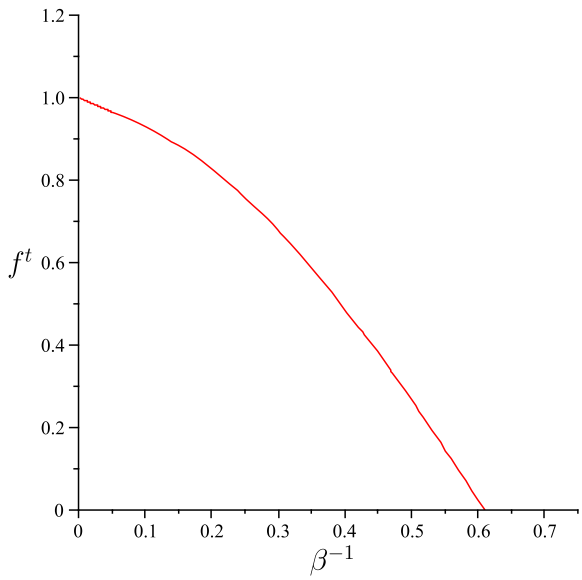


Figure 13. The temperature dependence of the critical force for the three-dimensional model in the $n \to \infty$ limit when the force is applied in the xy-plane at 45° to the x-axis.

Setting $\epsilon = -1$ gives a critical force of 1 at $T = 0$ and the limiting slope $\mathrm{d}f/\mathrm{d}T = -\log 2 < 0$.

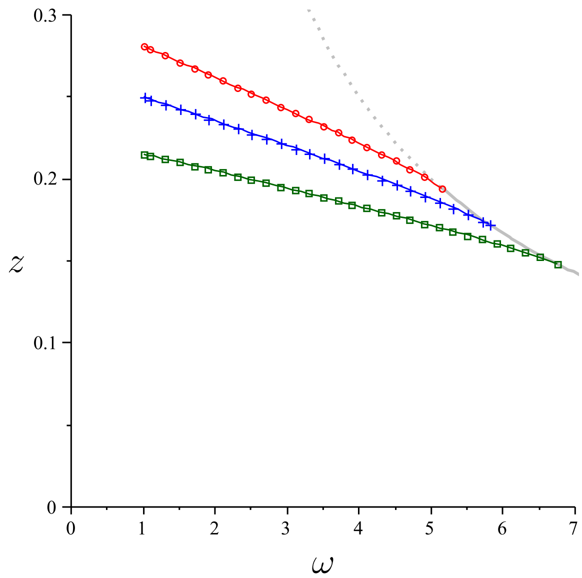


Figure 14. The boundary of convergence of the generating function as a function of ω for the three-dimensional model when the force is applied in the xy-plane at 45° to the x-axis. The rectangular hyperbola is independent of the value of $h_x = h_y$. The three curves with points marked correspond to $h_x = h_y = 1$ (top curve), $h_x = h_y = 1.2$ and $h_x = h_y = 1.5$.

9. Discussion

We have analysed the polymer model of partially directed walks with self-interaction, so as to induce a collapse transition, under the influence of tensile forces on the ends of the polymer. The problem of forces only in the preferred direction of the walk can be elucidated completely. The phase transition which is a second-order transition without any force is unchanged by the presence of such a force. The force extension curves at high temperatures look qualitatively similar to those of AFM experiments (Gunari *et al* (2007)).

The solution of the full model is more problematic. While the exact solution of the generating function of partition functions can be written down in terms of q-series, these functions are even more complicated than those encountered in the standard model that has only forces in the preferred direction (those are q-Bessel functions). We have been able to solve the model on the important special curve in parameter space which should contain the transition point. This seems to indicate that, again, the transition is unaffected by the force. This is more difficult to understand physically as the force must change the high temperature state of the polymer, unlike a force applied only in the preferred direction. It would therefore be interesting to analyse this full model further.

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