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A collapse transition in a directed walk model

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Abstract. We consider a directed walk model of linear polymers in dilute solution, with an energy associated with the number of near-neighbour contacts in the walk. For this model we can derive an exact expression for the generating function in two variables conjugate to the number of steps and the number of contacts. We discuss the analytic structure of this generating function and identify the transition corresponding to collapse.

1. Introduction

A self-avoiding walk on a regular lattice is a good model of the equilibrium properties of a linear polymer molecule in dilute solution in a good solvent. If near-neighbour interactions are suitably weighted the (infinite) walk is thought to undergo a transition which models the internal transition in a polymer brought about by the dominance of attractive forces between monomers at low temperatures. This transition has been studied theoretically for many years (see, e.g., Mazur and McCrackin 1968, Finsy *et al* 1975, Ishinabe 1985, Saleur 1986, Privman 1986, Chang *et al* 1988, Meirovitch and Lim 1989 and many other papers).

In this paper we consider a simpler variant of this model. We consider self-avoiding walks on the square lattice in which no steps are allowed in the west direction. If we are interested only in the number of n -step walks, this model is trivially easy to solve. However, if we require the number $c_n(m)$ of n -step walks with m near-neighbour contacts the problem is more difficult. An example of such a walk, illustrating the contacts, is shown in figure 1. This model, together with some variants, has been studied by a number of workers (Zwanzig and Lauritzen 1968, Lauritzen and Zwanzig 1970, Nordholm 1973, Veal *et al* 1990, Binder *et al* 1990). In particular, Binder *et al* used transfer matrix methods to show that the model has a phase transition, and located the critical point.

Our approach to the problem is quite different from that used by Binder *et al*. In section 2 we derive some rigorous results about the qualitative behaviour of the limiting free energy of this model. Then in section 3 we use a method originally suggested by Temperley (1956) to derive recurrence relations which determine the generating function $G(x, y)$ of $c_n(m)$ and solve these to obtain an expression for $G(x, y)$. In section 4 we investigate the analytic structure of G and, in section 5, we identify the location of the collapse transition.

This follows immediately from

$$\begin{aligned} Z_n(x_1)Z_n(x_2) &= \sum_{m_1} c_n(m_1)x_1^{m_1} \sum_{m_2} c_n(m_2)x_2^{m_2} \\ &\geq \left(\sum_m c_n(m)(x_1x_2)^{m/2} \right)^2 \\ &= [Z_n(\sqrt{x_1x_2})]^2 \end{aligned} \tag{2.6}$$

on taking logarithms, dividing by n and letting $n \rightarrow \infty$. Since $\kappa(x)$ is convex (and bounded above for finite x) it is continuous and has left and right derivatives at every $x < \infty$. Moreover, both derivatives increase with increasing x .

For $x \leq 1$ it follows from monotonicity that $\kappa(0) \leq \kappa(x) \leq \kappa(1)$ and hence that

$$\lim_{x \rightarrow 0^+} \kappa(x)/\log x = 0. \tag{2.7}$$

For $x \geq 1$ monotonicity implies that $\kappa(x) \geq \kappa(1)$. In addition

$$Z_n(x) \geq c_n(m_{\max})x^{m_{\max}} \tag{2.8}$$

where m_{\max} is the maximum number of contacts, for given n . Since the number of contacts will be maximal for a walk which ‘fills’ a square it is easy to see that $m_{\max} = n + o(n)$. Similarly, $c_n(m_{\max})$ is the number of Hamiltonian walks with n steps, with the restriction that no steps are allowed in the west direction. Clearly

$$\kappa(x) \geq \limsup_{n \rightarrow \infty} n^{-1} \log c_n(m_{\max}) + \log x. \tag{2.9}$$

By a similar argument

$$Z_n(x) \leq Z_n(1)x^{m_{\max}} \tag{2.10}$$

so that

$$\kappa(x) \leq \kappa(1) + \log x \tag{2.11}$$

and (2.9) and (2.11) imply that

$$\lim_{x \rightarrow +\infty} \kappa(x)/\log x = 1. \tag{2.12}$$

We shall find it convenient to define the generating function

$$\begin{aligned} G(x, y) &= \sum_{m, n} c_n(m)x^m y^n \\ &= \sum_n Z_n(x)y^n \\ &= \sum_n e^{\kappa(x)n + o(n)} y^n \end{aligned} \tag{2.13}$$

where we have used (2.4) to obtain the final result. At fixed x , $G(x, y)$ converges for $y < e^{-\kappa(x)}$ which defines a boundary in the (x, y) -plane. If we write this boundary curve as $y = y_c(x)$ then it follows from (2.12) that, for large x , $y_c(x) \sim x^{-1}$.

In the next section we shall derive an explicit expression for $G(x, y)$.

3. The form of the generating function

Let $c_n^r(m)$ be the number of walks with n steps and m contacts, with the first step in the east direction followed by precisely r steps in either the north or south direction. We define the generating function

$$g_r(x, y) = \sum_{m,n} c_n^r(m) x^m y^n \tag{3.1}$$

so that

$$G(x, y) = \sum_{r \geq 0} g_r(x, y). \tag{3.2}$$

We shall abbreviate $g_r(x, y)$ as g_r when no confusion is likely to occur. We can now write down recurrences for the g_r as follows:

$$g_0 = y + y(g_0 + g_1 + g_2 + \dots) = y + yG \tag{3.3}$$

and, in general, for $r \geq 1$

$$g_r = y^{r+1} \left(2 + \sum_{k=0}^r (1 + x^k) g_k + (1 + x^r) \sum_{k>r} g_k \right). \tag{3.5}$$

By eliminating terms we then derive the following recurrence relation

$$g_{r+1} - (1 + x) y g_r - (1 - x) x^r y^{r+2} g_r + x y^2 g_{r-1} = 0. \tag{3.6}$$

To solve this difference equation we define $q = xy$ and try the solution

$$g_r = \lambda^r \sum_{m=0}^{\infty} p_m(q) q^{mr} \tag{3.7}$$

with $p_0(q) = 1$. Substituting we find that this is a solution if

$$\begin{aligned} \lambda^2 - (y + q)\lambda + yq + \sum_{m=1}^{\infty} q^{mr} [p_m(q) \{ \lambda^2 q^{2m} - (y + q)\lambda q^m + yq \} \\ + p_{m-1}(q)(q - y)\lambda y q^m] = 0. \end{aligned} \tag{3.8}$$

This is satisfied if we take

$$\lambda^2 - (y + q)\lambda + yq = 0 \tag{3.9}$$

and

$$p_m(q) = \frac{\lambda(y - q) y q^m p_{m-1}(q)}{(\lambda q^m - y)(\lambda q^m - q)} \tag{3.10}$$

(provided that the denominator is not equal to zero). Equation (3.9) has two solutions $\lambda_1 = y$ and $\lambda_2 = q$. The recurrence relation (3.10) can be readily solved to give

$$p_m(q) = \frac{\lambda^m(y - q)^m y^m q^{m(m+1)/2}}{\prod_{k=1}^m (\lambda q^k - y)(\lambda q^k - q)} \tag{3.11}$$

and the general solution for g_r for $r > 0$ is

$$g_r = A_1 g_r^{(1)} + A_2 g_r^{(2)} \tag{3.12}$$

where A_1 and A_2 are arbitrary functions of y and q determined by the initial conditions and

$$g_r^{(i)} = \lambda_i^r + \lambda_i^r \sum_{m=1}^{\infty} \frac{\lambda_i^m (y - q)^m y^m q^{m(m+1)/2}}{\prod_{k=1}^m (\lambda_i q^k - y)(\lambda_i q^k - q)} q^{mr}. \tag{3.13}$$

To determine the value of A_2 we first note that if we fix $x > 1$ and $0 < y < 1$ such that $xy < 1/(1 + \sqrt{2})$, and then take the limit $r \rightarrow \infty$, then $\lim q^{-r} g_r^{(1)} = 0$, $\lim q^{-r} g_r^{(2)} = 1$ and $\lim q^{-r} g_r = 0$. It then follows from (3.12) that $A_2 = 0$.

To determine A_1 we proceed as follows. We note that equation (3.12) is valid only for $r \geq 1$. That is, g_0 is not a solution of (3.6) for $r = 0$. However, if we define h_0 to be $A_1 g_0^{(1)}$ then we note that $g_0 = \frac{1}{2} h_0$, so that

$$g_0 = \frac{1}{2} A_1 g_0^{(1)} = y + yG. \tag{3.14}$$

Similarly

$$g_1 = A_1 g_1^{(1)} = a + bG \tag{3.15}$$

where $a = y^2(2 + y - xy)$ and $b = y^2(1 + x + y - xy)$. Hence we have a pair of simultaneous equations in A_1 and G , which can be solved to give

$$G = \frac{2yg_1^{(1)} - ag_0^{(1)}}{bg_0^{(1)} - 2yg_1^{(1)}}. \tag{3.16}$$

Although we cannot use (3.16) to obtain a solution when $q = 1$, this is possible if we return to the recurrence relation (3.6). Thus, substituting $q = 1$ in (3.6) gives

$$G(1/y, y) = -1 + \sqrt{\frac{1 - y}{1 - 3y - y^2 - y^3}} \quad q = 1. \tag{3.17}$$

4. Analytic structure of $G(x, y)$

Since the analytic structure of $G(x, y)$ is related to that of $g_r^{(1)}$, we first consider this. It is convenient to work in the complex y -plane and so we consider G and g as functions of y with x fixed and real. We first note that the denominator of the l th term in $g_r^{(1)}$ is zero for $q^k = 1$ or $q^k = x$ (for $k = 1, \dots, l$). Thus for these values

of q , $g_r^{(1)}$ is infinite. The circle $|y| = 1/x$ is clearly a natural boundary, whilst it is straightforward to show that the points $y = \omega_p x^{k-1-1}$ ($k = 1, \dots, \infty$, $p = 1, \dots, k$, ω_p a k th root of unity) are isolated simple poles. The circle $|y| = 1/x$ is a set of accumulation points for these poles, all of which occur between the circles $|y| = 1$ and $|y| = 1/x$. For y not equal to any of these values the individual terms are finite and the D'Alembert ratio test shows that the series is convergent, so that $g_r^{(1)}$ is analytic in the remaining complex y -plane.

From now on we confine our attention to the real positive y -axis. The singularities of G on this axis are obtained by rewriting G in the form

$$G(x, y) = -\frac{aH(x, y) - 2y^2}{bH(x, y) - 2y^2} \quad g_1^{(1)} \neq 0 \tag{4.1}$$

where

$$H(x, y) = yg_0^{(1)}/g_1^{(1)}. \tag{4.2}$$

If $g_1^{(1)} = 0$ it is straightforward to show that G is not singular. G is singular at the zeros of the denominator (so long as these are not cancelled by corresponding zeros of the numerator) and at any singularity of the numerator (not cancelled by the denominator).

We now argue that, for fixed x , the point $y = 1/x$ is an accumulation point of zeros of the denominator of G and hence an accumulation point of poles of G . We have shown that, for y between $1/x$ and 1 , $g_0^{(1)}$ and $g_1^{(1)}$ both have $1/x$ as an accumulation point of simple poles. However, in H , the poles from $g_0^{(1)}$ cancel those from $g_1^{(1)}$ leaving H non-singular at the points $y = x^{k-1-1}$, $k = 1, \dots, \infty$. Instead, H has a pole at the zeros of $g_1^{(1)}$, which occur between each pair of adjacent poles of $g_1^{(1)}$ (i.e. at a point between $y = x^{k-1-1}$ and $y = x^{(k+1)-1-1}$, $k = 1, \dots, \infty$). Because the poles of $g_1^{(1)}$ have $1/x$ as an accumulation point, so must the zeros, and hence the poles of H must also have $1/x$ as an accumulation point.

For fixed x , the zeros of the denominator of G arise when $H = 2y^2/b$. A sketch, for y between 1 and $1/x$, of $2y^2/b$ and any function with $1/x$ as an accumulation point of poles, shows that the two plots intersect between each pair of adjacent poles. Thus the zeros of the denominator of G have $1/x$ as an accumulation point.

We now show that the denominator has no zeros in the domain $0 \leq y \leq 1/x$, $x > x_c$, where $x_c = 3.382975\dots$ (the solution to a cubic equation given later). For this we require a continued fraction representation of H . If we introduce a parameter t into $g_r^{(1)}$ as follows

$$g_r^{(1)}(t; x, q) = y^r + y^r \sum_{m=1}^{\infty} \frac{t^m x^{-m} (1/x - 1)^m q^{m(m+3+2r)/2}}{\prod_{k=1}^m (1 - q^k)(1 - q^k/x)}. \tag{4.3}$$

then it is straightforward to show that $g(t; x, q) \equiv g_0^{(1)}(t; x, q)$ satisfies the functional equation

$$g(t; x, q) - (1 + 1/x + (1/x - 1)q^2t/x)g(qt; x, q) + g(q^2t; x, q)/x = 0 \tag{4.4}$$

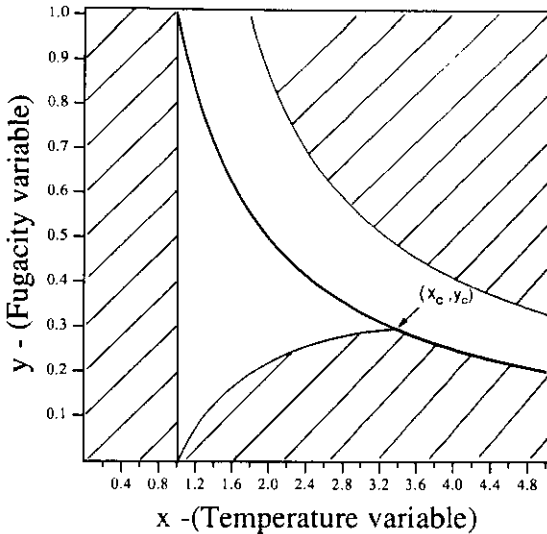


Figure 2. A sketch of the domain of convergence of the continued fraction.

which can be written in the form

$$H(t; x, q) = 1 + 1/x + (1/x - 1)q^2t/x - \frac{1/x}{H(qt; x, q)} \quad g(qt; x, q) \neq 0 \quad (4.5)$$

where $H(t; x, q) = g(t; x, q)/g(qt; x, q)$. Note that $H(1, x, q) \equiv H(x, y)$. Upon iteration (4.5) leads to a continued fraction. The domain of convergence of the continued fraction can be found using Worpitzky's theorem (Wall 1948). First the continued fraction is cast in the form

$$H(t; x, q) = (1 + 1/x + (1/x - 1)q^2t/x)(1 + b_1C) \quad (4.6)$$

where

$$C = \frac{1}{1 + \frac{b_2}{1 + \frac{b_3}{1 + \frac{b_4}{\ddots}}}} \quad (4.7)$$

and

$$b_{p+1} = \frac{-1/x}{(1 + 1/x + (1/x - 1)q^{p+2}t/x)(1 + 1/x + (1/x - 1)q^{p+3}t/x)} \quad (4.8)$$

The theorem states that the continued fraction C converges if

$$|b_{p+1}| \leq \frac{1}{4} \quad p = 1, 2, \dots \quad (4.9)$$

A careful investigation of (4.9) shows that C converges for those (real) values of x and y in the domain $\mathcal{D} = \{x \geq x_c\} \cap \{0 \leq xy \leq 1\}$. The domain of convergence is larger, and is sketched in figure 2.

To prove that the denominator of G has no zeros in the domain $0 \leq y \leq 1/x$, $x > x_c$, we use an additional result of Worpitzky's theorem, namely

$$|C - \frac{4}{3}| \leq \frac{2}{3}. \tag{4.10}$$

Thus, for C real we have $\frac{2}{3} \leq C \leq 2$ and hence, in the domain \mathcal{D} , we have

$$\begin{aligned} (1 + 2b_1)((1 + 1/x + (1/x - 1)q^2/x) \leq H(1; x, q) \\ \leq (1 + 1/x + (1/x - 1)q^2/x)(1 + 2b_1/3). \end{aligned} \tag{4.11}$$

The zeros of the denominator of G (in the form of (4.1)) are given by solutions of

$$H(x, q) = \frac{2}{1 + x + q(1/x - 1)}. \tag{4.12}$$

Thus, (4.11) gives a bound on the left-hand side of (4.12). It is then a simple matter of checking whether the range of the right-hand side intersects the range of the bounds. Using the monotonic nature of the functions and plotting a few points then shows that in the domain \mathcal{D} there is *no* intersection. Thus the zeros cannot occur in the domain \mathcal{D} .

The convergence of the continued fraction on the hyperbola $xy = 1, x > x_c$ shows that H , and hence G , must be finite here. This contrasts with the behaviour when the hyperbola is approached from above \mathcal{D} . The hyperbola is then the locus of a set of accumulation point of poles and hence switches between $+\infty$ and $-\infty$ with increasing frequency.

We can also use the continued fraction to show that, *on the hyperbola* $xy = 1$, the only points at which the denominator has a zero are $x = 1, y = 1$ and $x = x_c, y = 1/x_c$. As pointed out to us by Flajolet (private communication), if we formally take the limit $q \rightarrow 1$ then

$$H(t; x, 1) = 1 + 1/x + (1/x - 1)t/x - \frac{1/x}{H(t; x, 1)} \tag{4.13}$$

which is a simple quadratic equation for $H(t; x, 1)$. Thus,

$$\lim_{q \rightarrow 1} \frac{g_0^{(1)}}{g_1^{(1)}} = \frac{1}{2x} \left[1 + x^2 - (1 - x)^{1/2}(1 + x + 3x^2 - x^3)^{1/2} \right]. \tag{4.14}$$

Substituting into (4.12) gives

$$(x - 1)(x^3 - 3x^2 - x - 1) = 0. \tag{4.15}$$

This has two real solutions $x = 1$ and $x_c = 3.382975 \dots$. The solution $x = 1, y = 1$ is cancelled by a corresponding zero in the numerator and so we can discard it.

Three further zeros can be found exactly: when $x = 0$ and $y = 0.453397 \dots$ (a solution of $1 - 2y - y^3 = 0$) and when $x = 1$ and $y = -1 \pm \sqrt{2}$. Finally, a numerical solution of (4.12) shows that there is a line of zeros connecting the points $(0, 0.45, \dots)$, $(1, -1 + \sqrt{2})$ and $(x_c, 1/x_c)$. Numerically it becomes more difficult to find the line within a prescribed accuracy the closer one approaches the hyperbola $xy = 1$. However, in the next section we show that the line must meet the hyperbola at $(x_c, 1/x_c)$.

5. The collapse transition

The walk model considered here can be interpreted in a number of ways. We consider two possible interpretations. For the thermodynamics we can choose to have either two or three extensive thermodynamic variables, for instance the entropy S , the internal energy U with the third being the number of monomers N . We denote the thermodynamic number of monomers by N and the number of monomers in a particular walk by n . Since the walk is not confined to a box, we do not have a volume variable. If we choose two variables S and U , then we use n as a parameter. The thermodynamics of this system is then obtained from the statistical mechanics using the conventional canonical formalism, for which G is the generating function of the canonical partition function Z_n . In this case n plays the role of a parametric constraint on the size of the system and hence an n -step walk is then the analogue of a finite size system, and the thermodynamic limit is the limit $n \rightarrow \infty$.

If however the number of monomers, n is allowed to change then we must have three thermodynamic variables, with $N = \langle n \rangle$. In this case G becomes a *generalized* canonical partition function (Hill 1956), and the thermodynamic limit is the limit $\langle n \rangle \rightarrow \infty$. For finite $\langle n \rangle$ we again have the analogue of a finite size system.

In the thermodynamic limit, and under some general conditions, either formalism may be used as the averages are equal (Nordholm 1973). In the case of two variables, the radius of convergence of G gives us the canonical free energy in the thermodynamic limit (i.e. (2.13)), whilst in the case of three variables the radius of convergence of G occurs where $\langle n \rangle = \infty$ (see later). In the (x, y) -plane the locus of singularities of G closest to the x -axis gives a line which we refer to as the *thermodynamic limit boundary* or, more briefly, as the *boundary*.

We can show that $\langle n \rangle$ is infinite on the boundary as follows. The average value of n at a point (x, y) in the plane is given by

$$\langle n(x, y) \rangle = \frac{\partial \log G(x, y)}{\partial \log y}. \quad (5.1)$$

For $0 \leq y \leq e^{-\kappa(x)}$, $x \geq 0$, G can be written as

$$G(x, y) = \frac{F(x, y)}{1 - e^{\kappa(x)}y} \quad (5.2)$$

where $F(x, y)$ is analytic in this region, and hence

$$\langle n \rangle = yF'/F + ye^{\kappa(x)}/(1 - e^{\kappa(x)}y). \quad (5.3)$$

This means that $\langle n \rangle$ is infinite on the boundary and finite below it (since F has no zeros below the boundary).

The boundary is shown in figure 3. From the arguments in section 4, it is clear that the boundary starts at $(0, 0.453, \dots)$, passes through $(1, 0.414, \dots)$ and, because the free energy is continuous, the boundary must meet the hyperbola at $(x_c, 1/x_c)$. (It cannot pass below it as G has no singularities below the hyperbola and it cannot meet the hyperbola at $x < x_c$ because G is complex on the hyperbola for $x < x_c$.) Beyond this point the boundary coincides with the hyperbola.

As the boundary, which we denote by $y_c(x)$, corresponds to the thermodynamic limit, it is on this boundary that the collapse transition occurs. The phase transition corresponds to a point of non-analyticity of $y_c(x)$. Since the boundary is the hyperbola for $x \geq x_c$ and a different function for $x < x_c$, the function $y_c(x)$ is non-analytic with a singularity at x_c . Thus we identify $x_c = 3.3829757\dots$ as the position of the collapse transition.

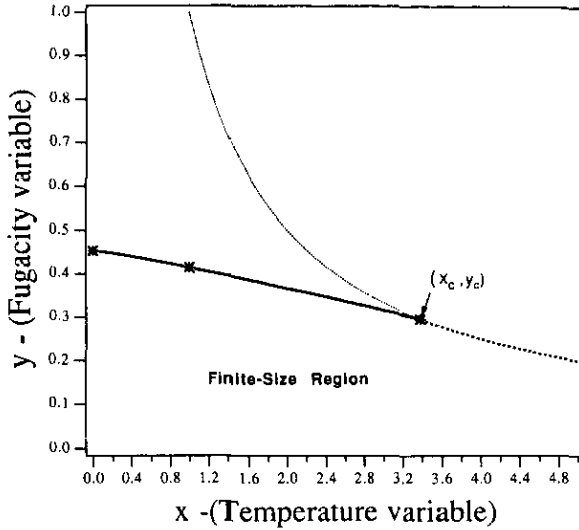


Figure 3. A plot of the fugacity variable y against the temperature variable x , showing the thermodynamic limit boundary before the collapse point (x_c, y_c) (full curve) and after the collapse point (bold broken curve) where it coincides with the hyperbola. The remaining part of the hyperbola is also shown (light broken curve). Exact points on the boundary are shown with an asterisk.

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