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Interacting partially directed walks: A model of polymer collapse

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A survey of the results that have been obtained to date on the partially directed walk model of the polymer collapse transition is presented.

We take this opportunity to present a brief history of partially directed walks as a solvable version of the more profound problem of self-avoiding walks and concentrate on them particularly as a model of polymer collapse. Models of polymer collapse in dilute solution have been explored since Flory [1] described his mean field theory of the θ-point in monodisperse solutions of a single polymer species. This θ-point is the temperature below which the polymer is in a collapsed state. Whereas, the configurations of polymers at high temperatures are dominated by the excluded volume effect. One focus of interest has been the scaling of properties with the length of the polymer. The idea that the large length limit of polymers is a critical phenomenon (some would say a self-organised one) was exploited by de Gennes [2] and des Cloizeaux [3] to provide scaling analyses of the quantities of interest. Lattice statistical mechanics has traditionally utilised self-avoiding walks to mimic the configurational complexity of polymers and added appropriate Boltzmann weights to introduce effective interactions between monomers. A single self-avoiding walk is then a model of a single polymer (that is, equivalent to a very dilute solution). Without interactions it is believed to reproduce the scaling behaviour of such a lone polymer in a good solvent or at high temperatures. However, because of the complexity it is difficult (if not impossible) to obtain rigorous results. In contrast, Duplantier and Saleur [4] have conjectured the θ-point exponents in two dimensions using sophisticated mappings.

Another line of attack has been to consider a subset of self-avoiding walk configurations which leads to manageable mathematics. Partially directed self-

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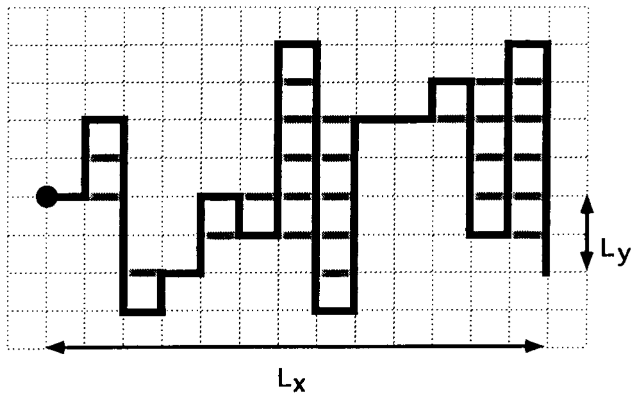

Fig. 1. A typical PDSAW with interactions in light grey between non-consecutive nearest-neighbour sites on the walk. Moving from left to right there are no steps in the negative x-direction and this property defines a PDSAW. The end-to-end distances (L_x and L_y) are marked.

avoiding walks (PDSAWs) are one such subset. Here we concentrate also on two dimensions. A partially directed walk is shown in fig. 1 where it can be seen that a PDSAW is a self-avoiding walk without any steps in the negative x-direction. These walks have been utilised in several contexts [5] since they can be conceived as domain walls in spin systems (solid-on-solid approximation [6]) as well as polymer configurations. The interactions are attractive nearest-neighbour ones between non-consecutive sites along the walk as shown in fig. 1.

This review is divided as follows. First, we give a concise history of the relevant works. Next we define, and state the solution of, the generalised partition function for the discrete and semi-continuous interacting PDSAW problem. Third, we sketch the behaviour of these functions and explain the phase diagram. The relevant exponent definitions are given and then the values calculated catalogued. We also state the connection between the generating functions of this model and a model previously examined by Zwanzig and Lauritzen and state further the results for the collapsed phase partition function scaling.

Without interactions PDSAWs have been studied extensively and this has been reviewed well by Privman [5]. This includes PDSAW in the presence of an attractive surface [7,8] that was examined by Privman, Forgacs and Frisch. The corresponding SOS model of wetting [9,10] has also received attention [11]. Work on the PDSAW model with self-interactions effectively goes back to Zwanzig, Lauritzen and Nordholm [12–14] as models of protein folding. However, they did not consider PDSAWs but walks that must fold back on themselves at every step. The SOS (semi-continuous) model related to PDSAWs with interactions was examined by Abraham and Smith [15] in the context of wetting. The discrete version was recently examined [16]. The wetting problem, however, considers a different ensemble to the polymer problem, and so results from both systems mentioned above are not directly applicable to interacting PDSAWs (IPDSAWs). The problem of IPDSAWs was introduced simultaneously by Yeomans [17] where the interest was in the competition with an attractive surface, Klein and Seitz [18] and Brak, Guttmann and Whittington, who examined the pure problem. Veal et al. [17] made some accurate numerical transfer matrix calculations and sketched a possible phase diagram in the presence of a surface. Klein and Seitz also made careful numerical transfer matrix calculations. Binder et al. [19] solved the transfer matrix problem along one line of the temperature–fugacity plane to obtain several exact results (without a surface). Brak et al. [20] rigorously proved the existence of the thermodynamic limit and the existence of the phase transition (θ-temperature). They solved for the generating function using a method introduced by Temperley [21] in terms of basic hypergeometric functions.

Many exact results have been deduced and numerical work accomplished in the surface problem by Foster [22–24] and Iglöi [25]. Recently, we have studied the IPDSAW on a fully infinite lattice (no surface) and found the length scale exponents associated with each phase and the critical exponents of the θ-point [26,27]. The semi-continuous version has been solved exactly and the exponents calculated [26]. In the discrete case, the exponents have been calculated using a plausible asymptotic expansion. The results for the length scale exponents have also been understood using physically appealing arguments at the θ-point [24]. Numerical work [27] has led to the conjecture of the scaling in general collapse problems [28]. Also, a different scaling form for the collapsed phase partition function of polymers was conjectured [29] and subsequently found to hold exactly for the IPDSAW model [30].

We shall now briefly describe the solutions of the discrete and continuous IPDSAW problems. Due to the directed nature of this problem, these configurations can be described in a natural way through the length r_i of vertical segments between two horizontal steps, measured in the positive y-direction. Thus, we associate to each configuration an N-tuple $(r_1, r_2, \ldots, r_N)$ corresponding to a configuration of total length $L = \Sigma_{i=1}^{N} |r_i| + N$.

The energy due to the nearest-neighbour interactions for each of these configurations is then

$$U(r_1, r_2, \ldots, r_N) = -J \sum_{i=1}^{N-1} \min(|r_i|, |r_{i+1}|)\, \Theta(-r_i r_{i-1})\,, \tag{1}$$

where $\Theta(x)$ is the Heavyside step function and we set $J = 1$ for convenience. The canonical partition function as a sum over all possible configurations of fixed length L is then

$$Q_L(\beta) = \sum_{N=1}^{L} \left(\sum_{|r_1|+|r_2|+\cdots+|r_N|=L-N} \exp[-\beta U(r_1, r_2, \ldots, r_N)] \right). \tag{2}$$

We get the generalised partition function by summing over all possible lengths,

$$G(z, \beta) = \sum_{L=1}^{\infty} z^L Q_L(\beta), \tag{3}$$

so that we have

$$Q_L(\beta) = \frac{1}{2\pi \mathrm{i}} \oint G(x, \beta) \frac{\mathrm{d}z}{z^{L+1}}. \tag{4}$$

The generating function $G(z, \beta)$ can be further generalised to include weights for horizonal x and vertical y steps. The expression for such a $K(x, y, \beta)$ can be derived by considering the generalised partition functions $K_r = K_r(x, y, \beta)$ for walks that start with a vertical segment of height r, so that

$$K(x, y, \beta) = \sum_{r=-\infty}^{\infty} K_r. \tag{5}$$

Then concatenating these walks gives a recursion relation for K_r as follows:

$$K_r = xy^{|r|} \left\{ 1 + \sum_{s=-\infty}^{\infty} \exp[\beta \min(|r|, |s|)\, \Theta(-rs)]\, K_s \right\}. \tag{6}$$

It also follows that

$$K_0 = x\{1 + K(x, y, \beta)\}. \tag{7}$$

The solution can then be found [20] by solving this recursion relation as

$$1 + K(x, y, \beta) = \frac{1 - \omega}{2H(x, x\omega, xy^2\omega(\omega - 1))/H(x, x\omega, xy(\omega - 1)) - (1 + \omega) - (1 - \omega)x}, \tag{8}$$

where $\omega = \exp(\beta)$ and $G(z, \beta) = K(z, z, \beta)$. The functions H are defined as

$$H(y, q, t) = \sum_{n=0}^{\infty} \frac{q^{\binom{n}{2}}(-t)^n}{(y; q)_n (q; q)_n}, \tag{9}$$

where we have used the standard notation

$$(x; q)_n = \prod_{m=1}^{n} (1 - xq^{m-1}) . \tag{10}$$

The function H is directly related to a basic hypergeometric function [31]

$$H(y, q, t) = {}_1\phi_1(0, y; q, t) , \tag{11}$$

which can be seen as the q-deformation of the more familiar hypergeometric function ${}_2F_1$.

In the semi-continuous model the vertical segments are allowed to take on real values ($r_i \in \mathbb{R}$) and the partition function is

$$Q_L(\beta) = \sum_{N=1}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}r_1 \cdots \int_{-\infty}^{\infty} \mathrm{d}r_N \, \delta\left(\sum_{i=1}^{N} |r_i| - L\right) \exp[-\beta U(r_1, \ldots, r_N)] , \tag{12}$$

where the Dirac delta function restricts the 'counting' to fixed length (equal to L) walks. The generating function is given analogously to the discrete case as

$$G(z, \beta) = \int_0^{\infty} \mathrm{e}^{-\zeta L} Q_L(\beta) \, \mathrm{d}L , \tag{13}$$

where $z = \exp(-\zeta)$. In this variant of the model the generating function can also be found via a similar route to the discrete case where one now must solve a differential equation. It is expressed [26] as a ratio of Bessel functions:

$$1 + G(z, \beta) = \varepsilon^{-1} \frac{J_\nu(\varepsilon\nu)}{J'_\nu(\varepsilon\nu)} , \tag{14}$$

where

$$\varepsilon = \left(\frac{4}{\beta}\right)^{1/2} \tag{15}$$

and

$$\nu = \frac{\beta}{\zeta - \beta} . \tag{16}$$

The critical value of β is $\beta_\theta = 4$ and for low temperatures, $\beta > \beta_\theta$, the radius of convergence is simply given by $\zeta_c = \beta$. We note that the continuous model and the discrete model can be directly related by taking the continuum limit. If the size of the edges of the lattices, a, is put explicitly into the equations of the discrete model, and the limit $a \to 0$ is taken then the semi-continuous model is obtained.

Given the expressions for $G(z, \beta)$ for the two variants, the phase diagram can be understood with the help of a singularity diagram of the temperature–fugacity (β–z) plane. Fig. 2 plots the radius of convergence $z_\infty(\beta)$ of the discrete model (the continuous model is similar). This is interesting because the radius of convergence of the generating function is related to the thermodynamic free energy ($f_\infty(T) = \lim_{L\to\infty} -(\beta L)^{-1} \ln Q_L(\beta)$) as

$$z_\infty(\beta) = \exp[\beta f_\infty(T)] . \tag{17}$$

It has been proved that there exists exactly one non-analyticity in the function $z_\infty(\beta)$ and hence a phase transition point. This point can be identified as the θ-point by considering the scaling of the average size of the walk for large L.

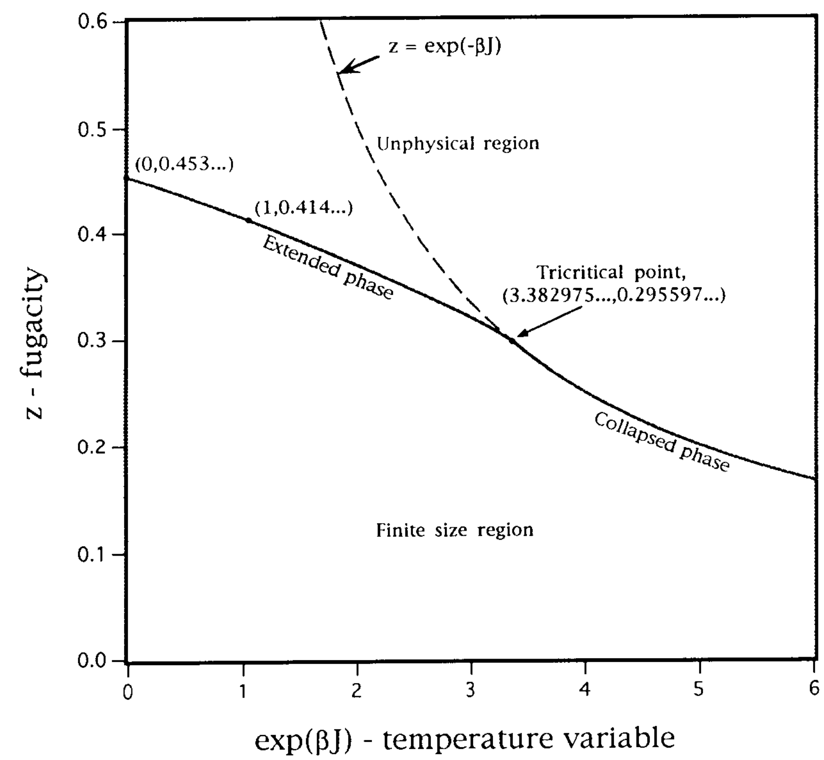

Fig. 2. The singularity diagram calculated from a continued fraction representation of the solution illustrating the radius of convergence ($z_\infty(\beta)$) of the generating function in the discrete model. The location of the critical (θ) point is shown and the dashed line indicates the analytic continuation of the low temperature manifold. Exponents are extracted by considering the singular part of the generating function on approaching the radius of convergence from below. The region $z < z_\infty$ can be identified as a finite length region in the generalised ensemble.

Three different scalings occur: one at high temperatures ($\beta < \beta_\theta$), one at β_θ and one at low temperatures. Moreover, the horizontal length scale decreases as the temperature decreases. It follows from the solution that the generating function satisfies a tricritical scaling form near β_θ. In both the discrete and continuous models the low temperature radius of convergence is particularly simple ($z_\infty(\beta) = \exp(-\beta)$) and it was on this curve that Binder et al. [19] solved the transfer matrix problem.

We will now discuss the values of the exponents for the IPDSAW problem. In anticipation, we reiterate a few known definitions. The asymptotic scaling form, in the length L of the chain, of the partition function, Q_L, for models of polymer collapse (θ-point) has usually been assumed to take the following form [3]:

$$Q_L \sim q_0 \mu^L L^{\gamma - 1} , \tag{18}$$

where $\ln \mu(\beta)$ is proportional to the temperature (β^{-1}) dependent free energy (also, $\mu(\beta) = z_\infty(\beta)^{-1}$). The exponent γ takes on a different value at the θ-temperature (γ^{t}) to that at high temperatures (γ^+).

At low temperatures, following fluid analogies, a Fisher droplet model type scaling has been suggested [29], which gives, in contrast,

$$Q_L \sim q_0 \mu_0^L \mu_1^{L^\sigma} L^{\gamma^- - 1} , \tag{19}$$

where σ and γ^- are expected to be universal exponents. Note that work on Hamiltonian walks [32,33] as models of dense polymers show a similar form in a different context.

Next, we give the definition of the size exponents via the end-to-end distance and radius of gyration. Because this is a directed problem, there are two length scale exponents that can be defined, each measuring the divergence of the average size of walks in the horizontal $\nu_\parallel$ and vertical directions $\nu_\perp$. These exponents are defined via the radius of gyration $\langle (R_{x,y})^2 \rangle^{1/2}(L)$, itself being an average (denoted by $\langle \cdot \rangle$) over the configurations of length L, as

$$\langle (R_{x,y})^2 \rangle \sim L^{\nu_{\parallel,\perp}} . \tag{20}$$

However, it is much easier to calculate the end-to-end distance (see fig. 1) exponents which are defined as

$$\langle L_{x,y} \rangle \sim L^{\nu_{x,y}} . \tag{21}$$

One can, however, calculate the average fold length associated exponent ν_{h} as a check on the vertical since one expects $\nu_\perp \geq \nu_h$. This is crucial at low temperatures. The horizontal exponents always satisfy $\nu_\| = \nu_x$.

The critical or θ-point yields additional exponents. The two most important are the thermal exponent α and the crossover exponent ϕ. Since the shape of the radius of convergence directly gives information about the canonical free energy, an exponent α describing the singular part of the free energy near T_θ can be calculated from the definition

$$f_\infty^{\text{singular part}}(T) \sim t^{2-\alpha} , \tag{22}$$

where $t = (T - T_\theta)/T_\theta$. We define the crossover exponent such that quantities of interest near the θ-point depend on the scaling combination tL^ϕ. This exponent is equal to the ratio of any pair of exponents derived from the same quantity in the two scaling directions. A shape exponent ψ can be immediately deduced since $\psi = 2 - \alpha$. A critical exponent for the surface free energy can be defined as

$$|1 - \mu_1(\beta)| \sim \text{const.} \times |\beta - \beta_\theta|^\chi . \tag{23}$$

Exponents can be found from a thermal correlation length on approaching the critical point along the thermal scaling axis and these are denoted with a superscript u as opposed to the fixed temperature exponents that gain a superscript t at the θ-point.

We shall now summarise the exponents as calculated or deduced from scaling. At high temperatures the exponents are those of free PDSAWs [5]. The expected results $\nu_x = \nu_\|$ and $\nu_y = \nu_\perp > \nu_h$ hold. Table I gives the values of the exponents.

At the θ-temperature, thermodynamic exponents arising from the thermal critical point also exist and hence there is an extended set of exponents. These are given in table II and can be understood with reference to the definitions above. Here also $\nu_\perp = \nu_y$ and in addition these are equal to ν_h.

Table I
High temperature exponents.

Exponent	γ	ν_x	ν_y	ν_h
Value	1	1	1/2	0

Table II
Tricritical exponents.

Exponent	γ^t	γ^u	ν_x^t	ν_y^t	ν_h	ν_x^u	ν_y^u	α	ϕ	ψ	χ
Value	1/3	1/2	2/3	1/3	1/3	1	1/2	1/2	2/3	3/2	3/4

At low temperatures the size exponents are difficult to compute exactly but can be found to high numerical accuracy. The point worth mentioning is that here the radius of gyration and end-to-end distance exponents differ. Since $\nu_y < \nu_\perp$, the model does have some pathological behaviour. However, this can be understood in terms of a bubble picture [27] as $\nu_h = \nu_y$.

As mentioned above, the collapsed phase partition function scaling can be calculated exactly [30] in a straightforward application of the methods of Abraham and Upton [34,35]. Here we note the illuminating work of these authors on the bubble model (an SOS model) of ferromagnetic correlations and the essential singularity at first order transitions in such systems. Returning to walks, the calculation of the collapsed phase partition function confirms the conjecture made in [29] at least for this directed model. The asymptotics of the continuous solution below the critical temperature give

$$Q_L(\beta) \sim q_0 \, e^{\beta L} \mu_1^{L^{1/2}} L^{-3/4} , \tag{24}$$

with

$$q_0(\beta) = \left(\frac{2\beta^3 f}{\pi^2(\beta - 4)^2}\right)^{1/4} \tag{25}$$

and

$$\mu_1(\beta) = \exp[-(8\beta f)^{1/2}] , \tag{26}$$

where $f(\beta)$ is given as

$$f = \ln\left(\frac{\beta^{1/2} + (\beta - 4)^{1/2}}{2}\right) - \left(\frac{\beta - 4}{\beta}\right)^{1/2} . \tag{27}$$

We can then compare this directly with the conjectured form (19) to give the values quoted in table III.

Finally, when the IPDSAW model was studied previously, the similarity of the models discussed by Zwanzig and Lauritzen [12,13] to the IPDSAW was

Table III
Low temperature exponents.

Exponent	σ	γ^-	ν_x	ν_y	ν_h
Value	1/2	1/4	1/2	1/4	1/2

noticed. The models can be formally written down in similar fashion and it is clear that due to the different set of configurations considered the models differ somewhat. It has been shown that some of the exponents are the same and in fact while solving the continuous version the *same* differential equation occurs. The tantalising similarities can be explained by showing that one set of problems follow from the other using a necklacing [36,37] argument. The major difference between the models is that in the Zwanzig and Lauritzen (ZL) models the configurations are such that at each horizontal step the walk is constrained to fold back onto itself. For the discrete model it can be shown [26] that the generating functions of the ZL model (G^{zl}) and that of the IPDSAW model (G^{pd}) are related as

$$G^{\mathrm{pd}}(x, y; \beta) = \frac{2G^{\mathrm{zl}}(x, y; \beta) - x[1 + G^{\mathrm{zl}}(x, y; \beta)]}{1 - \{G^{\mathrm{zl}}(x, y; \beta) - x[1 + G^{\mathrm{zl}}(x, y; \beta)]\}}\,. \tag{28}$$

A similar expression exists for the continuous model.

We have seen in this review that many results have been obtained for the PDSAW model of an interacting polymer and indeed it is a rich model. The thermodynamic limit exists and the free energy has been computed. There exists the analogue of the θ-point where the polymer collapses by undergoing a continuous transition. This point is mathematically equivalent to a tricritical point in accordance with the de Gennes scheme and the well-known exponents can all be calculated (or at least found to high accuracy) in each phase. Progress has been made by Yeomans, Foster and colleagues towards the elucidation of a multicritical system when surface interactions are introduced as well as internal attractions. Here, however, no exact generating function is known. It would be fascinating to find such a function. In any case, since the thermodynamic limit is not known to exist even for infinite temperature isotropic walks this directed model has yielded much useful information to date.

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