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# Two-dimensional self-avoiding walk with hydrogen-like bonding: phase diagram and critical behaviour

D P Foster<sup>1</sup> and F Seno<sup>2</sup>

<sup>1</sup>Laboratoire de Physique Théorique et Modélisation (CNRS ESA 8089), Université de Cergy-Pontoise, 5 Mail Gay-Lussac 95035 Cergy-Pontoise Cedex, France

<sup>2</sup>INFN–Dipartimento di Fisica, Università di Padova, Via Marzolo 8, 35131 Padova, Italy

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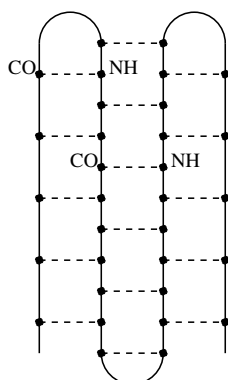
## Abstract

The phase diagram for a two-dimensional self-avoiding walk model on the square lattice incorporating attractive short-ranged interactions between parallel sections of walk is derived using numerical transfer matrix techniques. The model displays a collapse transition. In contrast to the standard  $\theta$ -point model, the transition is first order. The phase diagram in the full fugacity–temperature plane displays an additional transition line, when compared to the  $\theta$ -point model, as well as a critical transition at finite temperature in the Hamiltonian walk limit.

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## 1. Introduction

Self-avoiding walks have been widely studied as models of polymers in dilute solution [1]. A self-avoiding walk on a lattice is defined as a random walk which is forbidden from visiting the same lattice-site more than once [1]. In the limit of very long walks it models a polymer in a good solvent. In order to model the relative affinity between the monomers (compared with the solvent) an attractive energy is introduced between non-consecutively visited nearest-neighbour sites [2, 3]. This is the standard  $\theta$ -point model. At high temperatures the polymer is happy to be in solution. As the temperature is lowered the polymer tends to collapse in on itself, and at a given temperature will precipitate from solution. For an idealized infinitely long polymer the high temperature and low temperature regimes are separated by a phase transition occurring at a temperature known as the theta temperature,  $T_\theta$ , [1, 4, 5]. In the grand canonical description the average length of the walk is controlled by a fugacity  $K$  (or chemical potential  $\mu$  where  $K = \exp(-\beta\mu)$ ). At high temperatures the (average) length of the walk



**Figure 1.** A schematic representation of hydrogen bonds in a beta sheet (From Bascle *et al* [11]).

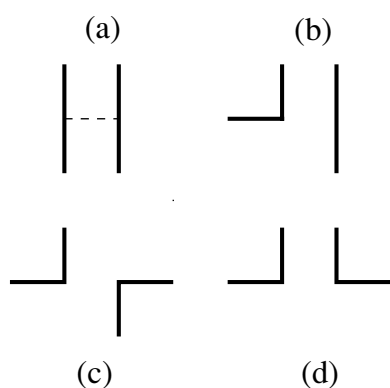
diverges smoothly as a critical fugacity  $K_c(T)$  is approached. At low temperatures the length jumps discontinuously at a given value of the fugacity  $K^*(T)$  (corresponding to a first-order transition). The two lines  $K_c(T)$  and  $K^*(T)$  follow continuously one from the other, and the two behaviours are separated by a tricritical point, at a temperature corresponding to  $T_\theta$ . The transition line  $K_c(T)$  then  $K^*(T)$  is identified with the ‘thermodynamic limit’ of the polymer problem. Along this line, the proportion of visited sites is zero for  $T < T_\theta$  and becomes non-zero continuously for  $T > T_\theta$ .

While it is clear that the main experimental interest lies in three dimensions (although there are some experimental results also in two dimensions [6]), there has been a lot of theoretical interest in the two-dimensional case [7–9]. This is in part due to the fact that the upper critical dimension for a tricritical point is three [10]. In dimensions lower than three (but larger than one) there is a possibility for a greater diversity of critical behaviours.

In this paper we investigate a two-dimensional model with a restricted set of interactions, compared to the theta model; an interaction is only present between nearest-neighbour non-consecutively visited sites belonging to straight portions of polymer, i.e. an interacting site cannot sit on a corner of the walk (see figure 2). This choice of interactions may be motivated by the rôle of hydrogen bonding in the formation of secondary structures in proteins [11]. These bonds are formed between the CO group of one peptide and the NH group of a nearby (non-consecutive) peptide. This bond imposes a constraint on the orientation of the relevant peptides. This type of bonding is thought to be responsible for the formation of alpha helices and beta sheets [12]. In our two-dimensional toy-model the formation of alpha helices is not possible. A representation of the formation of a beta sheet through hydrogen bonding is shown in figure 1.

Our main interest in this paper is not to give a realistic model for protein folding, but rather to understand the influence of these apparently small modifications to the local attractive interactions on the critical behaviour of lattice interacting self-avoiding walks. To this end we present the phase diagram and elucidate the critical behaviour in the full fugacity–temperature plane.

In section 2 we present in detail the model as well as the transfer matrix calculation of the quantities of interest. In section 3 we present the phase diagram and discuss the different transitions present. In section 4 we concentrate more specifically on the Hamiltonian walk limit of the model in which all sites are visited exactly once. In section 5 we finish with some concluding remarks.



**Figure 2.** Possible configurations of nearest-neighbour non-consecutively visited sites. Configurations of type (a) include an attractive interaction energy  $-\epsilon$ , configurations of types (b), (c) and (d) interact in the standard  $\theta$ -point model, but here do not participate in hydrogen type bonding.

## 2. The model and the transfer matrix calculation

The model studied here consists of a self-avoiding walk embedded on a square lattice. An interaction energy  $-\epsilon$  is assigned for each non-consecutively visited pair nearest-neighbour sites for which the four bonds are parallel (see figure 2). A chemical potential,  $\mu$ , and related fugacity  $K = \exp(-\beta\mu)$  are associated to each step.

The grand canonical partition function is then

$$\mathcal{Z} = \sum_{\text{walks}} K^N \exp(\beta N_I \epsilon) \quad (1)$$

where  $N$  is the number of steps in the walk and  $N_I$  is the number of interactions. Quantities of interest may be calculated as appropriate derivatives of the partition function, for example, the density is given by

$$\rho = \frac{\langle N \rangle}{\Omega} = \frac{K}{\Omega} \frac{\partial \log \mathcal{Z}}{\partial K} \quad (2)$$

where  $\Omega$  is the number of lattice sites. The relative length fluctuations are related to the derivative of  $\rho$  through

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{K}{\rho} \frac{\partial \rho}{\partial K}. \quad (3)$$

In the dilute polymer regime (small enough  $K$ ) the correlation function may be identified with the probability that two given points are joined by a walk. In this case the correlation length must scale in the same way as any reasonable characteristic length scale associated to the walk. It is usual to take the radius of gyration, which corresponds to the average squared distance the walk steps from the common centre of gravity. It follows that

$$R_G \sim |K - K_c|^{-\nu} \quad (4)$$

where  $\nu$  is defined as the standard correlation length exponent [13]. Using the relation (2), one finds

$$R_G \sim \langle N \rangle^\nu \quad (5)$$

from which we may see that the walk is fractal; the mass of the walk scales linearly with  $N$ , and hence  $R_G^{1/\nu}$ . The fractal (Hausdorff) [14] dimension of the walk is then  $d_H = 1/\nu$  [1]. It

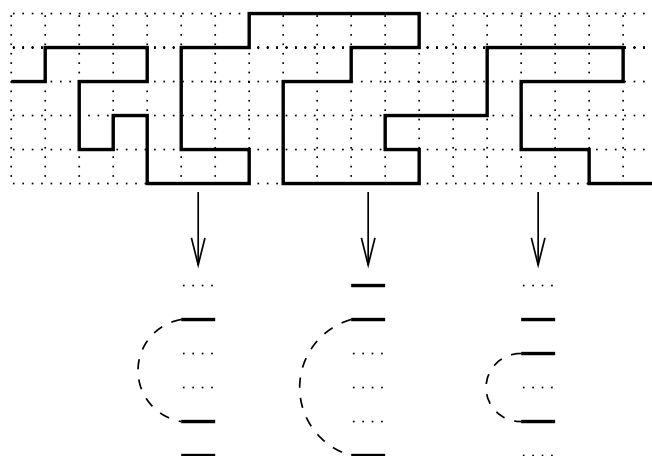


Figure 3. Example of a polymer configuration with the corresponding column states.

is usual in such problems to take equation (5) as the definition of the exponent  $\nu$  [1]. In this case, note that it only relates to the usual critical exponent in the case of a critical transition in the dilute regime. In the collapsed phase(s) the polymer fills the lattice, the mass scales as  $R_G^d$  and equation (5) gives  $\nu = 1/d$ .

In this paper we propose to use a transfer matrix formalism to calculate  $\mathcal{Z}$  as a function of  $K$  and  $\beta\epsilon$  [15–17]. For convenience we shall from now on set  $\epsilon = 1$ , which simply corresponds to a choice of temperature scale.

The idea behind the transfer matrix formalism is to calculate the partition function on a lattice which is infinite in one direction (the  $x$  direction, say) but finite in the other ( $y$ ) direction. The thermodynamic limit is attained by increasing the lattice width.

The standard way of considering the problem is as follows: Define the restricted partition function  $Z_x(\mathcal{C}_0, \mathcal{C}_x)$  as the partition function for a portion of walk between the origin and  $x$ . The walk has a column state  $\mathcal{C}_0$  at the origin and  $\mathcal{C}_x$  in column  $x$ . One may then write the following recursion relation:

$$Z_{x+1}(\mathcal{C}_0, \mathcal{C}_{x+1}) = \sum_{\mathcal{C}_x} Z_x(\mathcal{C}_0, \mathcal{C}_x) \mathcal{T}(\mathcal{C}_x, \mathcal{C}_{x+1}) \quad (6)$$

where  $\mathcal{T}(\mathcal{C}_x, \mathcal{C}_{x+1})$  is the additional Boltzmann weight to add column  $x + 1$  in configuration  $\mathcal{C}_{x+1}$  next to column  $x$  in configuration  $\mathcal{C}_x$ . This forms a (transfer) matrix.

That this recursion should be valid for a spin system is fairly straightforward, since the interactions are all local. For a polymer model it is less clear that this should be possible, since one has to take into account non-local factors, most notably one has to ensure that the partition function describes only one chain, without the formation of ‘orphan’ loops. This is done by appropriately defining the column states  $\mathcal{C}_x$ . For the self-avoiding walk problem with no added interactions (i.e.  $\epsilon = 0$ ) it is sufficient [15] to define a column configuration by the arrangement of horizontal bonds in the column along with information about the connectivities between the bonds, that is information about which pairs of horizontal bonds are connected by polymer loops to the left (taking  $x$  as increasing towards the right). See figure 3 for an example. By successive application of (6), one finds

$$Z_x(\mathcal{C}_0, \mathcal{C}_x) = \langle \mathcal{C}_0 | \mathcal{T}^x | \mathcal{C}_x \rangle. \quad (7)$$

The situation becomes a little more complicated if interactions are to be taken into account. It is necessary to know the column states over three columns in order to incorporate the horizontal bonds. The appropriate modification to the above equations is [16, 18]

$$Z_{x+1}(C_0, C_1; C_x, C_{x+1}) = \sum_{C'_{x-1}, C'_x} Z_x(C_0, C_1; C'_{x-1}, C'_x) T(C'_{x-1}, C'_x; C_x, C_{x+1}) \quad (8)$$

and

$$Z_x(C_0, C_1; C_{x-1}, C_x) = \langle C_0, C_1 | T^{x-1} | C_{x-1}, C_x \rangle. \quad (9)$$

The primed configurations are introduced to retain the matrix notation, the elements of the matrix are now labelled by the two column states for the input and two for the output (primed), with the restriction that only matrix elements with  $C_x = C'_x$  may be non-zero.

It is required that the partition function sum over walks of all possible lengths. To do this we define a restricted partition function  $\mathcal{Z}_x$  for all the walks having a caliper extension  $x$ , i.e. walks which are entirely confined to a strip of length  $x$ , and extend over the entire length of the strip. This is simply  $Z_x$  summed over all configurations  $C_0, C_1, C_{x-1}$  and  $C_x$  compatible with the starting and ending configurations of the walk. The full partition function is then given by

$$\mathcal{Z} = \sum_{x=0}^{\infty} \mathcal{Z}_{x+1} \quad (10)$$

$$= \sum'_{b.c.} \sum_{x=0}^{\infty} T^x \quad (11)$$

where the primed sum is over the boundary configurations, as described above.

Let us denote the eigenvalues of  $T$  by  $\{\lambda_i\}$ , numbered in the order of their moduli. The eigenvalue of largest modulus,  $\lambda_1$ , is always positive.

For small enough  $K$ ,  $\lambda_1 \leq 1$ . In this case the partition function may be written as

$$\mathcal{Z} = \sum_i \frac{\alpha_i}{1 - \lambda_i(K, \beta\epsilon)}. \quad (12)$$

The  $\alpha_i$  are essentially constants dependent on the boundary conditions, which gives for the density

$$\rho = \frac{K}{\Omega} \sum_i \frac{1}{1 - \lambda_i} \frac{\partial \lambda_i}{\partial K}. \quad (13)$$

If the derivative of  $\lambda_i$  is finite, which is the case at least for small enough  $\beta$ , the density is zero as long as  $\lambda_1 < 1$  and may only change from its zero value when the average length of the walk diverges, i.e.  $\lambda_1 \geq 1$  [17, 18]. The point  $\lambda_1 = 1$  is identified with the critical transition, and is often used in polymer science to define the ‘thermodynamic limit’ of ‘very long’ polymers [1]. Another way of reaching the same conclusion is to consider two points as being correlated if they are joined by a walk. One may then identify  $Z_x$  with a two-point correlation function, and hence identify the correlation length,  $\xi$  [17],

$$\xi = \frac{1}{\log\left(\frac{1}{\lambda_1}\right)}. \quad (14)$$

The correlation length diverges as  $\lambda_1 \rightarrow 1$ , consistent with the identification of a critical transition.

The above argument needs to be treated with caution. As long as the lattice width is finite, the system is equivalent to a one-dimensional system with a finite, if large, number of states

per site (each site corresponding to a column in our model). It is well known that a one-dimensional system with a finite number of states per site cannot have an equilibrium-phase transition<sup>1</sup>.

The reason for this apparent discrepancy is that the definition of  $\xi$  (14) is not valid in the large  $K$  phase (dense polymer phase). In a spin model the partition function would have been given by  $\mathcal{Z}_x$  in the limit  $x \rightarrow \infty$ . The transfer matrix would contain all the possible configurations, and a standard analysis shows that [20]

$$\xi = \frac{1}{\log\left(\frac{\lambda_0}{|\lambda_1|}\right)} \quad (15)$$

where  $\lambda_0$  is the largest eigenvalue and  $\lambda_1$  is the second largest (in modulus). To ensure the correct construction of a single walk all configurations consisting of an empty column have been excluded from the transfer matrix, but replaced by the sum over all possible polymer extensions  $x$ . The consequence of this choice is that the largest eigenvalue in the zero-density phase has been eliminated. Its value, as can be seen by inspection of the expression for  $\xi$ , would be  $\lambda_0 = 1$ .

This prescription only holds as long as  $\lambda_1 < 1$ . If  $\lambda_1 > 1$  then the partition function, density and  $\xi$  are given by

$$\mathcal{Z} \sim \lim_{x \rightarrow \infty} \lambda_1^x \quad (16)$$

$$\rho = \frac{K}{L\lambda_1} \frac{\partial \lambda_1}{\partial K} \quad (17)$$

$$\xi = \frac{1}{\log\left(\frac{\lambda_1}{|\lambda_2|}\right)} \quad (18)$$

where  $L$  is the lattice width.

For convenience we impose the condition that the walk of extension  $x'$  in the  $x$  direction originates at  $x = 0$  and terminates either at  $x = 0$  or  $x = x'$ . As is usual in equilibrium phase transitions, the precise choice of boundary condition does not change the critical behaviour. Imposing this restriction it is easy to see that column configurations with even numbers of horizontal bonds may only follow column configurations with even numbers of horizontal bonds, and likewise for configurations with an odd number of horizontal bonds. This block diagonalization is convenient since it transpires that for much of the phase diagram  $\lambda_1$  and  $\lambda_2$  arise in different blocks. It is relatively easy to calculate the largest eigenvalues of a matrix using the power method [21].

### 3. The $K$ - $\beta$ phase diagram

The critical lines may be identified using phenomenological renormalization [22]. At a critical point the correlation lengths for two strip widths, measured as a fraction of the strip width, must be the same. This reflects the scale invariance of a critical system. In practice, a finite width system is always off-critical, however,

$$\frac{\xi_L(K^*)}{L} = \frac{\xi_{L'}(K^*)}{L'} \quad (19)$$

gives a finite-size estimate of the critical fugacity,  $K^*$ , which will tend to the true critical fugacity as the strip widths tend to infinity. Assuming that the system is sufficiently close to the true critical point, the correlation length behaves (to leading order) as

$$\xi_L = A|K^* - K_c|^{-\nu}. \quad (20)$$

<sup>1</sup> This follows directly from a Peierls type argument, see for example [19].

Since it is the finite width of the system which prevents the correlation length from diverging, at  $K^*$  we have  $L \propto \xi_L$ . If these two scaling laws are admitted, then a finite-size estimate of the correlation length exponent may be calculated from the equation:

$$\frac{1}{\nu_{L,L'}} = \frac{\log\left(\frac{d\xi_L/dK}{d\xi_{L'}/dK}\right)}{\log\left(\frac{L}{L'}\right)} - 1. \quad (21)$$

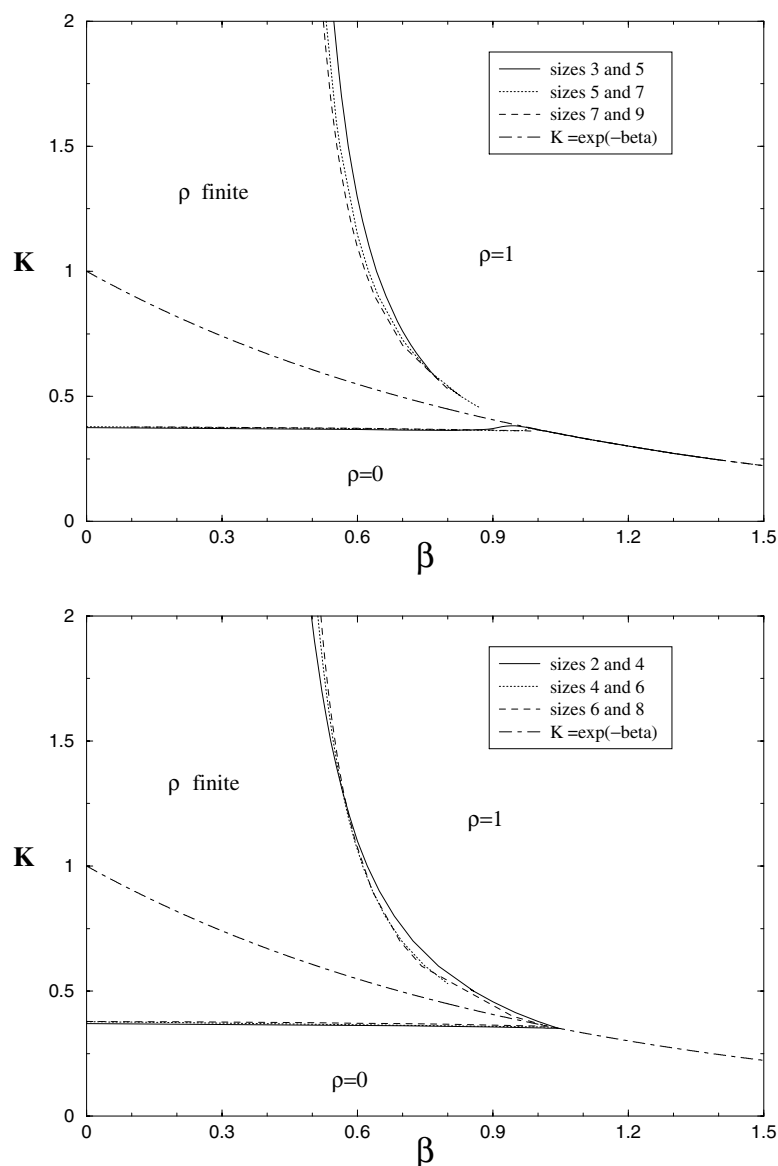
There exists at least one phase transition. In the case  $\beta = 0$  this corresponds to the standard self-avoiding walk transition. As  $\beta$  is increased, this point extends into a line of critical points. In analogy to the standard  $\theta$ -point model, we would expect this transition to change to first order at some given value of  $\beta = \beta_H$ . As discussed in the previous section, starting from the low- $K$  phase, the correlation function is given by (14). In the high- $K$  phases the appropriate form of  $\xi$  is given by (15). The phase diagram estimates found with phenomenological renormalization, using the appropriate form of  $\xi$ , are shown in figure 4. As is usual in this sort of problem, there are strong parity effects, notably for the odd lattice widths  $\lambda_1$  is in the odd sector of the transfer matrix, while for the even lattice widths  $\lambda_1$  is taken from the even sector. The next largest eigenvalue,  $\lambda_2$ , is in the other sector for the low- $K$  phase and for the high temperature high- $K$  phase, while it is in the same sector for the high- $K$  low temperature phase. This observation was not used to estimate the transition lines, which were however found assuming that  $\lambda_1$  and  $\lambda_2$  came from different sectors of the transfer matrix. Not all the transition lines are found for even lattice widths.

Let us now characterize the different phases and transitions. For low  $K$  the average length of the polymer is finite and the density of the polymer on the lattice must therefore be zero. The first transition as  $K$  is increased is to one of two dense phases, depending on whether  $\beta < \beta_H$  or  $\beta > \beta_H$ . It is convenient to use the density as an order parameter. For practical reasons we choose boundary conditions in which the polymer is made to extend the length of the lattice, between  $x = 0$  and  $x \rightarrow \infty$ . This obliges the polymer to be infinite in length even in the zero-density phase. A choice of boundary conditions is not expected to affect the critical behaviour of an equilibrium system. The partition function becomes  $\mathcal{Z} = \lim_{x \rightarrow \infty} \lambda_1^x$  for both the high and low density phases, and  $\rho$  may be calculated using (17) in all phases. The density will now be finite for  $K < K_c$  as long as the lattice width is finite, but must tend to zero as  $L \rightarrow \infty$ . This is indeed what is observed from the density plots shown in figures 5 and 6.

As expected, for  $\beta < \beta_H$  the behaviour of  $\rho$  and the length fluctuations indicate the existence of a line of second-order phase transitions. The line is in the self-avoiding walk universality class, having  $\nu = 3/4$  as may be seen from the finite-size estimates for  $\nu$  shown in figure 7. The transition is to a finite-density phase.

For  $\beta > \beta_H$  the density plot, given in figure 6, indicates that the transition is first order to a dense phase. That this line corresponds to the compact polymer state is confirmed by the observed exponent  $\nu = 0.5 = 1/d$  (figure 7). A major difference with the  $\theta$ -point model, seen using the phenomenological renormalization scheme is the existence of two different high density phases. The density plots in figure 6 for  $\beta > \beta_H$  suggest that the walk changes discontinuously from  $\rho = 0$  to  $\rho = 1$ , and that the density of interactions saturates instantly. In other words the lattice changes abruptly from being essentially empty to essentially full, with a maximum density of interactions. Trivially, a lattice which is empty (a finite walk length on an infinite lattice) has zero energy and zero entropy per site; the free energy per site is zero. If the lattice is completely full with the interactions density saturated, the walk may only be in one of two configurations; either all the bonds are vertical or all the bonds are horizontal. The entropy per site in this phase is therefore also zero. Since, in this state, there is one bond and one interaction per site, the energy per site is  $e = \mu - \epsilon$ . The transition between the two

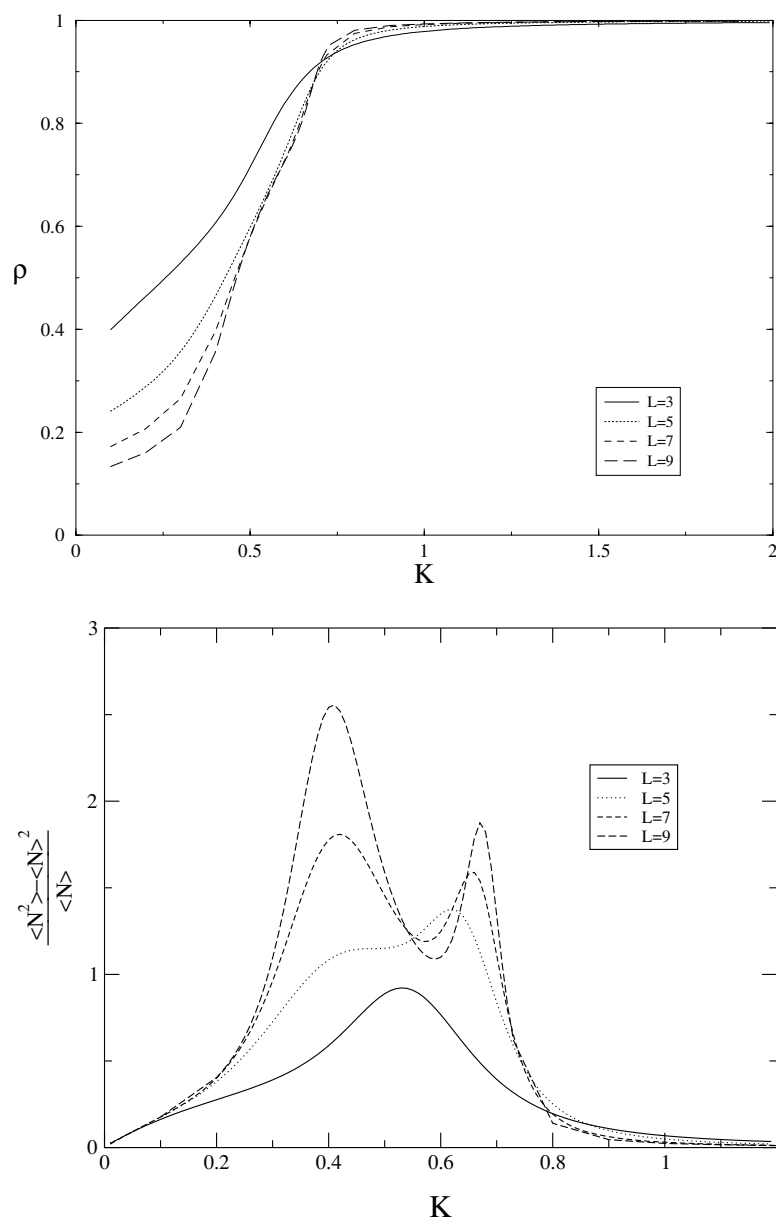




**Figure 4.** Phase diagram estimates found using phenomenological renormalization group for odd lattice widths (top) and even lattice widths (bottom).

phases would then occur when the free energy per site,  $f = e - Ts = e = 0$ , in other words when  $\mu = \epsilon$ . Recalling the choice of  $\epsilon = 1$ , the transition line would be  $K = \exp(-\beta)$ . This line has been plotted for comparison on the phase diagrams, shown in figure 4. The agreement with the observed first-order transition line is excellent.

In order to differentiate between the two high density phases, it is convenient to use the interaction density,  $\rho_I$ , as an order parameter. This order parameter, along with its fluctuations, is plotted as a function of  $\beta$  for  $K = 1.5$  in figure 8. The order parameter differentiates between the two phases since it is identically one in the high- $\beta$  phase, and less than one in the low- $\beta$  phase. The variation of the order parameter appears to be fairly smooth for all lattice sizes,



**Figure 5.** Plots of density,  $\rho$ , (top) and density fluctuations (bottom) for the inverse temperature  $\beta = 0.7$ .

and leads one to conjecture that this high density transition is critical. Also plotted in figure 8 is the specific heat, calculated as the second derivative of the free energy with respect to the temperature, keeping  $\mu$  and  $\epsilon$  constant.

Various estimates of the critical  $\beta$  for  $K = 1.5$ , calculated using the phenomenological renormalization group and by locating the peaks in the specific heat, are given in table 1.

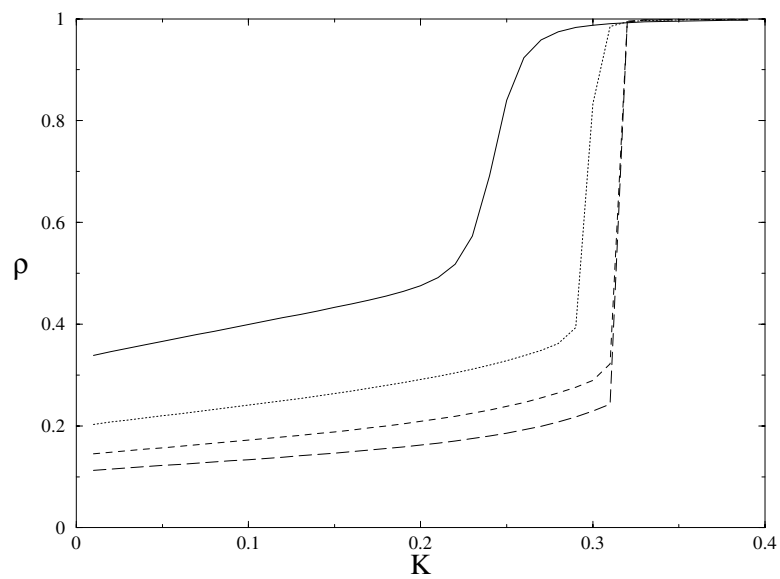


Figure 6. Plot of density  $\rho$  for  $\beta = 1.1$ .

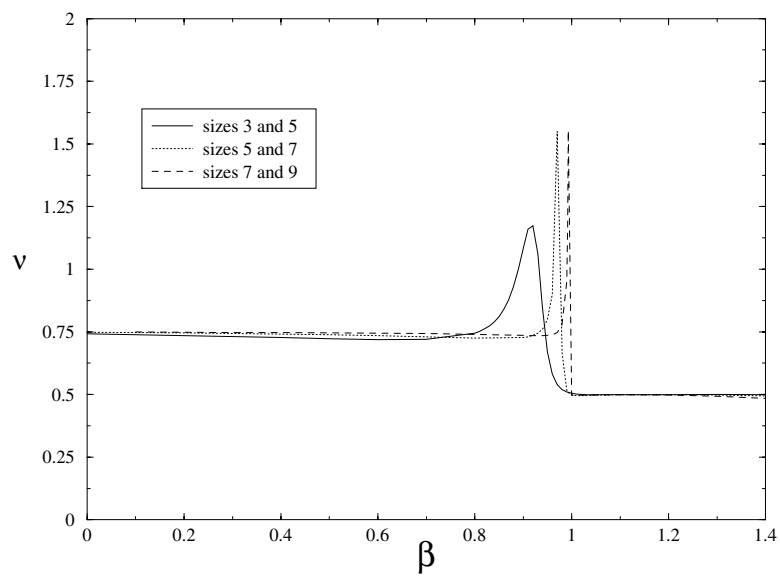
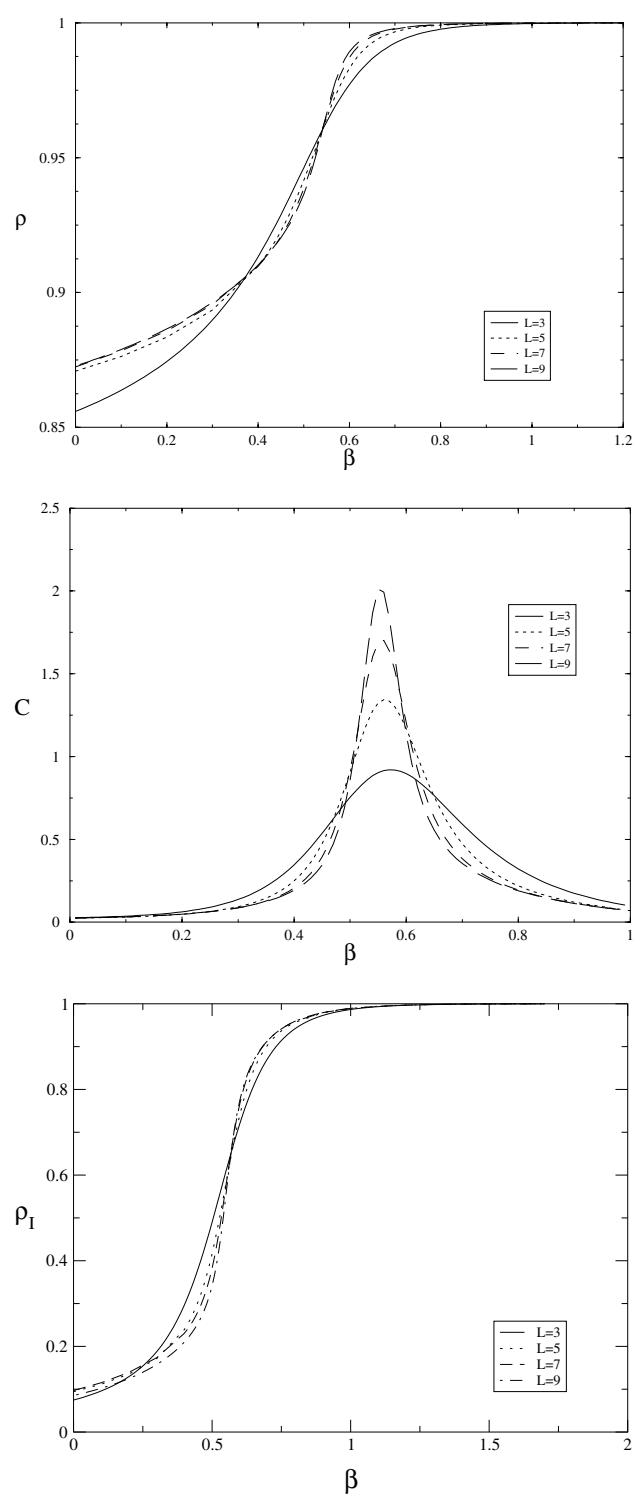


Figure 7. Estimates for the exponent  $\nu$  for the low- $K$  transition line.

The various results are coherent with an estimate  $\beta_c(K = 1.5) = 0.55 \pm 0.01$ . At a critical transition, the specific heat diverges as  $T \rightarrow T_c$  with an exponent  $\alpha$ ,

$$C \sim |T - T_c|^\alpha. \quad (22)$$



**Figure 8.** Plots of the density,  $\rho$ , (top), the specific heat,  $C$ , (middle) and the density of interactions,  $\rho_I$ , (bottom) for  $K = 1.5$ .

**Table 1.** Estimates for (a)  $\beta_c$  and  $\nu$  for  $K = 1.5$  limit using phenomenological renormalization group with strips of width  $L$  and  $L + 2$  and (b)  $\beta_c$  as estimated from the peak of the specific heat and the height of the peak.

$L$	(a)		(b)	
	$\beta_c$	$\nu$	$\beta_c^L$	$C_{\max}$
3	0.579 774	0.885 482	0.572 447	0.920 518
4	0.546 148	0.920 203	0.500 045	0.645 603
5	0.560 960	0.841 050	0.561 950	1.344 506
6	0.550 013	0.920 194	0.510 141	1.131 212
7	0.554 531	0.864 167	0.556 259	1.706 669
8	–	–	0.524 612	1.494 860
9	–	–	0.553 865	2.024 505

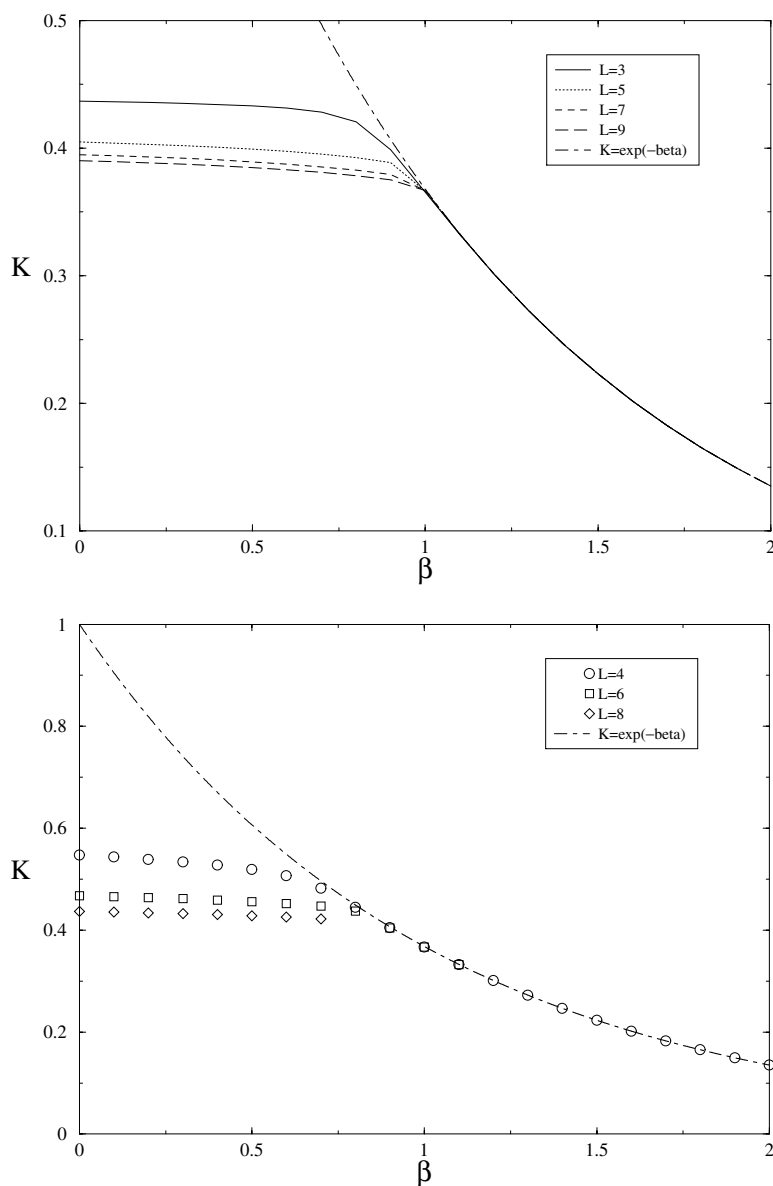
When combined with relation (20) and  $\xi_L \propto L$ , this leads to the finite-size scaling result

$$C_{\max} \approx A + BL^{\alpha/\nu}. \quad (23)$$

A three-point fit for odd widths gives  $\alpha/\nu = 0.67$  for  $L = 3, 5, 7$  and  $\alpha/\nu = 0.55$  for  $L = 5, 7, 9$ . A similar three-point fit for the even sizes,  $L = 4, 6, 8$  gives a value of  $\alpha/\nu = 0.156$ . If sufficiently large lattice widths are considered then  $A$  can be dropped. When this is not the case, then the result is an effective value of the exponent, which should converge to the correct value as the lattice width is increased. Unfortunately, the number of two-point approximations we could construct does not allow for meaningful extrapolation. All we could determine is that  $0.156 \leq \alpha/\nu \leq 0.55$  gives a reasonable limit on the possible values of  $\alpha/\nu$ . Using the scaling relation  $\alpha = 2 - d\nu$ , this gives  $\nu$  as  $0.78 \leq \nu \leq 0.93$ . Note that this range is coherent with the values of  $\nu$  found from the phenomenological renormalization group calculation, shown in table 1. Additionally, the upper boundary, calculated from the even lattice sizes, is in good agreement with the even lattice size estimates of  $\nu$  in table 1.

It now remains to determine the nature of the transition at  $(K_H, \beta_H)$ , where the three transition lines join. For the standard  $\theta$ -point model, this point is tricritical, and corresponds to the confluent of two transition lines, not three.

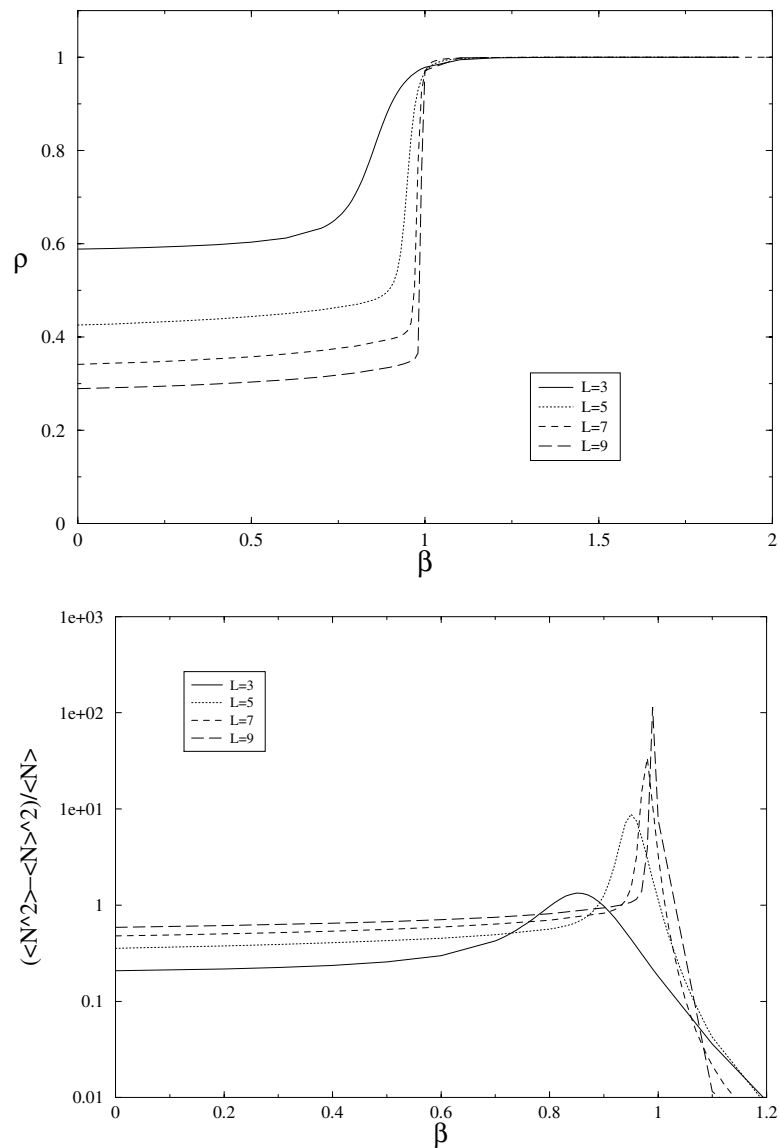
The problem we are faced with is that the phenomenological renormalization group applied to even lattice widths does not give the first-order transition at all. When applied to the odd lattice widths, the method is not able to follow the self-avoiding walk transition line all the way to  $\beta_H$ , jumping to the upper transition line just short of  $\beta_H$ . This undershoot rapidly becomes smaller as the lattice width is increased. Recalling that the length of the walk first diverges when  $\lambda_1 \rightarrow 1$  and that this condition coincides with the low- $K$  phase transitions in the thermodynamic limit, we can use the condition  $\lambda_1(K, \beta) = 1$  as a criterion for defining finite-width estimates to the transition lines. The phase diagram estimates calculated using this criterion are shown in figure 9. This method is incapable of giving the high- $K$  transitions, and converges more slowly than the phenomenological renormalization group, but has the advantage that the transition lines are fairly smooth and continuous. The density and its fluctuations, calculated along this line, are presented in figure 10. As the width of the lattice is increased, the jump in the density becomes sharper. The height of the fluctuations (shown with a log-linear scale in figure 11) increases extremely rapidly with lattice width, strongly suggesting a delta peak in the thermodynamic limit. Whilst the range of lattice widths prevent



**Figure 9.** Phase diagram estimates calculated using the condition that the largest eigenvalue  $\lambda_1 = 1$  odd lattice widths (top) and even lattice widths (bottom).

us from being categorical, the results suggest strongly that the transition is first order along the transition line. This seems to be confirmed in the phase diagram. In both figures 4 and 9 the transition line has a discontinuous slope at  $\beta_H$ .

The positions of the peaks of density fluctuations are shown in figure 11 along with the positions of the cusps where the upper and lower critical lines join for even lattice widths. We estimate  $\beta_H = 1.00 \pm 0.02$ , with  $K_H = \exp(-\beta_H)$ . It is strange that  $\beta_H$  should be

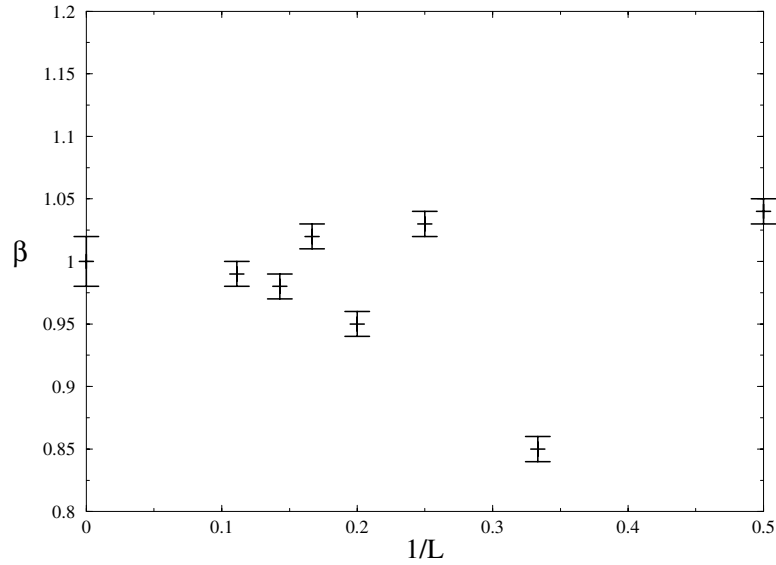


**Figure 10.** Density (top) and density fluctuations (bottom) along the transition line as estimated using the condition that the largest eigenvalue  $\lambda_1 = 1$ .

so close to one, though we have as yet not been able to determine why this should be the case.

#### 4. The Hamiltonian walk limit ( $K \rightarrow \infty$ )

In the limit  $K \rightarrow \infty$  the walk will fill the lattice maximally. Each site will be visited once only. In this limit the walk becomes what is known as an Hamiltonian walk [24]. The effect of



**Figure 11.** Finite-size estimates of  $\beta_H$ , the value of  $\beta$  at the collapse transition. The upper points, calculated for even lattice widths, come from the estimated position at which the two critical lines merge. The lower points, calculated for the odd lattice sizes, come from the peaks of the fluctuations in  $N$ . The error bars given correspond to the interval between the points calculated. These error bars could be reduced at an additional cost in computer time.

this interaction in this limit is to energetically penalize corners in the walk. This is similar to the Flory model [26] except that there are configurations which introduce one or two corners into the walk with no difference in energy (figure 2).

There is a low temperature corner-free phase. As the temperature is raised there is a transition in which the density of corners becomes non-zero. To distinguish between the high and low temperature phases it is possible to use either the density of corners or the energy density. This latter is shown as a function of  $\beta$  in figure 12.

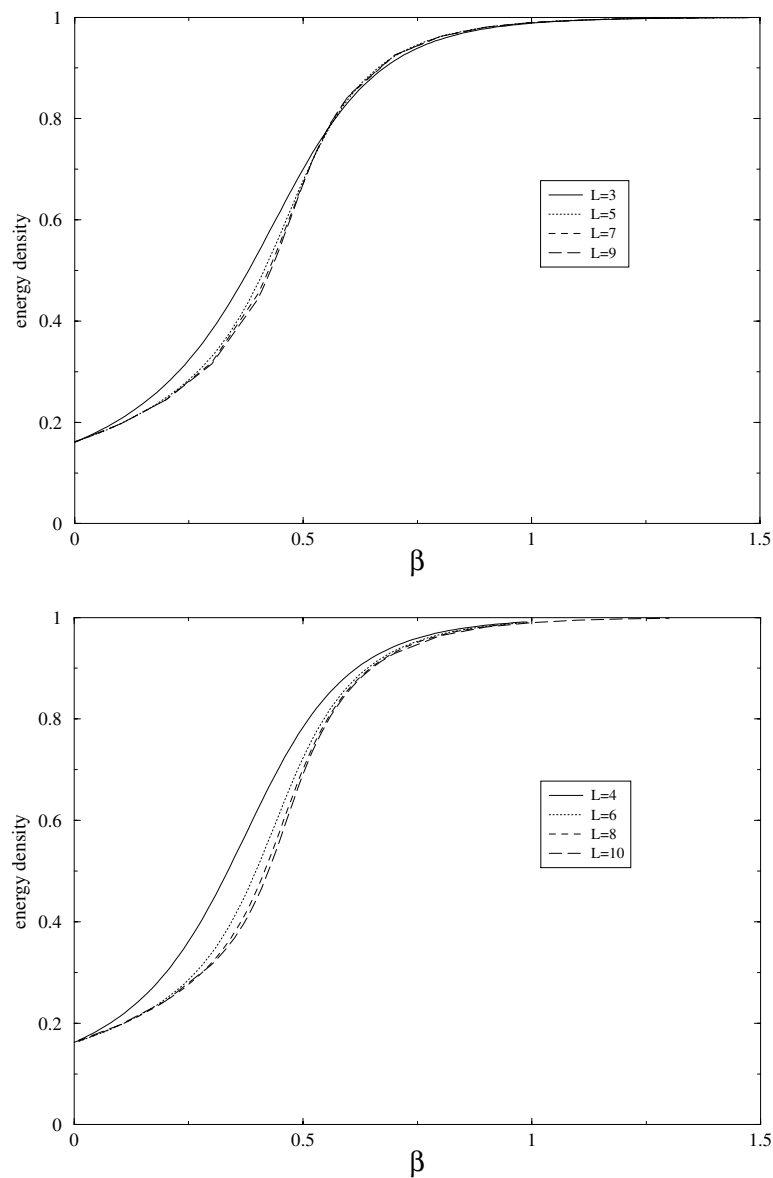
We estimate the critical temperature again using the phenomenological renormalization group, the results of which are shown in table 2 and extrapolated using a three-point fit to

$$\beta_c^\infty = \beta_c^L + AL^B \quad (24)$$

where  $\beta_c$  is the finite-size estimate and  $\beta_c^\infty$  is the extrapolated value.  $A$  and  $B$  are constants to be determined.

Only the odd lattice widths presented solutions to the phenomenological renormalization group equation (19), given in table 2. The positions and values of the maxima of the energy fluctuations per site, shown in figure 13, are also reported in table 2. The fluctuations appear to saturate. We assume that, even if the fluctuations do not diverge, the transition point is estimated by the value of  $\beta$  for which the fluctuations are maximal. This agrees well with the phenomenological renormalization group estimate, and fits with a continuation of the finite  $K$  phase diagrams (figure 4) to high values of  $K$ . Phenomenological renormalization and the peaks of the energy fluctuations give estimates of the critical temperature which concur, giving  $\beta_c = 0.476 \pm 0.001$ .





**Figure 12.** Energy density as a function of  $\beta$  in the  $K \rightarrow \infty$  limit for odd lattice widths (top) and even lattice widths (bottom).

It is also possible to estimate the exponent  $\eta$ , using the conformal invariance result for periodic boundary conditions [23]

$$\eta = \frac{L}{\pi\xi}.$$

We find  $\eta_c = 0.096 \pm 0.002$  (table 2).

It is anticipated that the entire high temperature phase is critical, in analogy with other models of this type, such as the model F [25], the Flory model [26] and the loop gas model on

**Table 2.** Estimates for (a)  $\beta_c$ ,  $\nu$  and  $\eta$  in the  $K \rightarrow \infty$  limit using phenomenological renormalization group with strips of width  $L$  and  $L + 2$  and (b)  $\beta_c^L$ , the critical value of  $\beta$  as estimated from the peak of the interaction fluctuations, the height of the peak ( $f_{\max}$ ) and the value of  $\eta$  calculated the extrapolated value of  $\beta_c$ . Even and odd lattice widths are taken apart.

$L$	(a)			(b)		
	$\beta_c$	$\nu$	$\eta$	$\beta_c^L$	$C_{\max}$	$\eta(\beta_c^\infty)$
3	0.450 472	1.109 084	0.082 484	0.435 221	1.714 121	0.087 226
4	–	–	–	0.375 742	1.875 099	0.035 357
5	0.461 359	1.060 628	0.085 672	0.465 233	2.124 762	0.090 245
6	–	–	–	0.437 435	2.260 666	0.047 824
7	0.465 970	1.105 916	0.087 611	0.471 160	2.354 970	0.092 053
8	–	–	–	0.454 834	2.491 249	0.056 830
9	–	–	–	0.473 274	2.492 086	0.093 240
10	–	–	–	0.461 866	2.636 003	0.064 064
$L \rightarrow \infty$ (odd)	0.477	–	–	$0.476 \pm 0.001$	2.867	$0.096 \pm 0.002$
$L \rightarrow \infty$ (even)	–	–	–	$0.473 \pm 0.003$	3.071	$0.10 \pm 0.01$

the brickwork lattice [27]. The estimates of  $\nu$  are not at all clear. They seem close to  $\nu = 1$ , but in other respects the transition is similar to that seen in the model F and the Flory model, which have transitions of infinite order with  $\nu$  infinite.

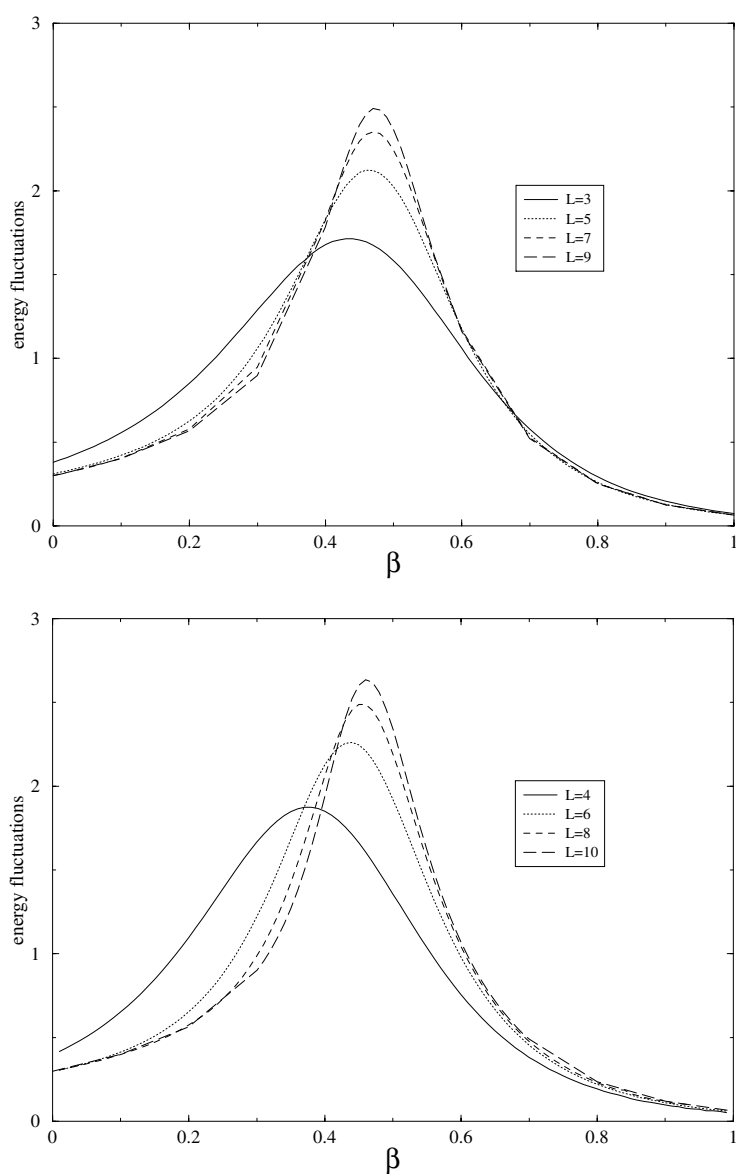
## 5. Conclusions

In this paper we have presented a two-dimensional model for homopolymer collapse under the influence of ‘hydrogen-bonding’ like nearest-neighbour interactions. The phase diagram is quite different from the equivalent  $\theta$ -point phase diagram; the collapse transition is now first order. This is also observed in the oriented interacting self-avoiding walk model, where, for appropriate values of the model parameters, a first-order collapse occurs to a spiral configuration [28]. These two models have in common that the collapsed phase is anisotropic, in our case one of the two lattice directions is selected, and in the oriented walk case, for strong enough parallel interaction strength, one of the two chiralities is selected. In the standard  $\theta$  model the collapsed phase is isotropic.

Here we also observe an additional transition in the dense walk regime. This transition appears to be second order, though for the moment we have not been able to determine to any accuracy any of the critical exponents. Similar critical lines are observed in the loop models with corner interactions, with or without a collapse transition [27, 29].

There also exists a non-trivial critical behaviour in the  $K \rightarrow \infty$  limit, where there is a finite-temperature phase transition between a critical high temperature phase and a frozen low temperature phase.

Another well-studied model with a qualitatively similar phase diagram is the partially directed interacting polymer model [30, 31]. There are major differences however: The line  $K = \exp(-\beta)$  corresponds to a phase transition line for all values of  $K$ , delimitating a similar fully collapsed phase. The equivalent phase to the finite- $\rho$  phase has a density  $\rho = 0$  due to the directed nature of the model. The equivalent to the  $\theta$ -point transition is second order [30]. (here it appears to be first order.)



**Figure 13.** The energy fluctuations in the  $K \rightarrow \infty$  limit for odd lattice widths (top) and even lattice widths (bottom).

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