1992

Lattice Statistics Of Polymer Adsorption

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by

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Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
April 1992

ISBN 0-315-75355-2

Canada

Abstract

The interaction of branched polymers with an adsorption surface is studied using rigorous and numerical methods. For a polymer network with a fixed topology and consisting of self-avoiding chains, we prove that the reduced free energy is the same as that for self-avoiding walks interacting with a surface. For a network modelled by a lattice animal, we prove that a phase transition exists when such an animal interacts with a surface. The transition points are numerically studied by one and two variable Padé approximants. A number of rigorous results for the statistics of lattice animals are also obtained.

Acknowledgements

I would like to thank my supervisor Dr. T. Lookman for his efforts and help in the preparation of this work. Particularly, I am grateful to Dr. T. Lookman for his excellent guidance and generous support over the last few years. I also wish to thank Dr. K. De'Bell for numerous discussions and, in particular, help with the Padé analysis.

Finally, I wish to express my sincere thanks to my wife, Dong Wei, who has offered continuous love and encouragement in the past five years. Her love has supported me to accomplish this dissertation.

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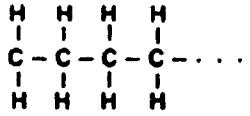
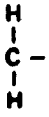
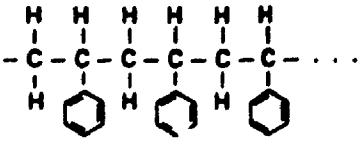
Introduction

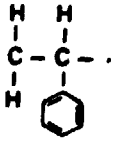
1.1 Statistics of polymer conformations

A linear polymer is a long chain molecule formed by the repetition of a basic unit or segment named as monomer. Examples of synthetic linear polymers are

polymethylene 

whose repeat unit is 

and polystyrene 

whose repeat unit is 

A polymer chain can have any number of monomers. The characteristic feature of such a linear polymer in dilute solution is its flexibility. This is primarily a result of its ability to rotate, relatively freely, about the backbone of the chain consisting of carbon-carbon covalent bonds. This rotational freedom allows the polymer chain to take up numerous conformations characterised by the dihedral angles about these bonds (De Gennes [1]).

The study of polymer conformations falls into two aspects:

(i) Local properties: conformations and motions of one monomer inside the chain and their dependence on chemical substitutions in the side group.

(ii) Global properties: dependence of physical properties (observables) on chain length, concentrations and a few basic interaction parameters.

The local features are essential whenever we want to choose an optimal polymer for a given practical application. This is the aspect studied by physical chemists.

The global point of view is the focus of this thesis. Here the details of the chain structure are omitted as much as possible to extract simple, universal features which will remain true for a large class of polymer chains. These features depend on n, the number of monomers of a chain, and are described by certain scaling laws for large n, represented by taking the limit $n \to \infty$. This is the aspect studied in critical phenomena. Moreover, we shall consider polymers in a dilute, good solution. The "dilute" refers to the fact that polymers are independent of each other and therefore, do not interact in any way. The term "good solution" is used to imply that the attraction between the monomers and solvent molecules is greater than the monomer-monomer interaction.

1.1.1 Random walks

The simplest model of a linear polymer is to regard it as a random walk on a lattice. The walk is a succession of n steps. At each step, the next jump may proceed to any of the nearest neighbour vertices, and statistical weight for these possibilities is the same. Such a walk is represented by a sequence of lattice vertices $\mathbf{W} = \{\mathbf{x}(0), \mathbf{x}(1), \ldots, \mathbf{x}(n)\}$ where $\mathbf{x}(i)$ and $\mathbf{x}(i+1)$ are a pair of adjacent lattice vertices. If each lattice vertex has z neighbours, the number of distinct possibilities at each step is z, and the total number of distinct n-step walks is z^n. The important quantities in studies of polymer solutions are the mean-squared end-to-end distance $\langle R^2 \rangle$ and

the mean-squared radius of gyration $\langle S^2 \rangle$ about the centre of mass of the chain. This latter quantity is of particular interest since the radius of gyration of a polymer in dilute solution is experimentally determinable, e.g. by light scattering experiments. They are defined by

$$\langle R_n^2 \rangle = \langle (\mathbf{x}(n) - \mathbf{x}(0))^2 \rangle, \tag{1.1}$$

and

$$\langle S_n^2 \rangle = \langle \frac{1}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{n} (\mathbf{x}(i) - \mathbf{x}(j))^2 \rangle, \tag{1.2}$$

where $\langle \cdot \rangle$ denotes an average over all n-step walks. For random walks, it can be shown that for large n,

$$\langle R_n^2 \rangle \sim n, \tag{1.3}$$

and

$$\langle S_n^2 \rangle = \frac{1}{6} \langle R_n^2 \rangle \tag{1.4}$$

(Barber and Ninham [2]).

A major problem with the random walk model is that it ignores the hard-core repulsion between the monomers far apart along the polymer chain which, in certain conformations, can be close together in space. This feature (the exclusion of one monomer from the region of space occupied by another) is called the *excluded-volume effect*. This effect destroys the Markovian nature of the problem, since a long term memory effect is implied. The standard model of linear polymers with excluded-volume effect is a self-avoiding walk (SAW) model. This is a random walk on a lattice with the restriction that a lattice vertex, once visited, cannot be revisited during the realization of the walk. The self-avoiding constraint represents the excluded-volume effect. This simple additional constraint generates a sufficiently difficult mathematical problem that few rigorous results are available.

The first rigorous result on the large n behaviour of the number of distinct self-

avoiding walks was obtained by Hammersley [3]. He showed that

$$\lim_{n\to\infty} \frac{1}{n} \ln c_n = \lim_{n\to\infty} \frac{1}{n} \ln p_n = \kappa, \tag{1.5}$$

where c_n denote the number of n-step SAW's with fixed $\mathbf{x}(0)$ and p_n denotes the number of n-step polygons which are SAWs with $\mathbf{x}(0) = \mathbf{x}(n)$. The limit κ is called *connective* or *effective* constant (note that some authors refer to $\mu = exp(\kappa)$ as the connective constant). It is widely believed that

$$c_n \sim e^{n\kappa} n^{\gamma-1}, \tag{1.6}$$

and

$$p_n \sim e^{n\kappa} n^{-2+\alpha}. \tag{1.7}$$

Although nothing analytic is known about the behaviour of $\langle R^2 \rangle$ and $\langle S^2 \rangle$ for a self-avoiding walk, numerical studies suggest, that for large n,

$$\langle R_n^2 \rangle \sim n^{2\nu}, \tag{1.8}$$

$$\langle S_n^2 \rangle \sim n^{2\nu}. \tag{1.9}$$

Numerical results indicate that $\nu = 0.75$ for $d = 2$ and $\nu = 0.59$ for $d = 3$.

Self-avoiding walks in restricted geometries can model polymers in restricted environments such as pores or capillaries. One of the questions which has attracted attention is how the geometrical constraints effect the asymptotic behaviour of the number of distinct self-avoiding walks. A number of rigorous and numerical results have been obtained for SAW's with geometrical constraints. For instance, consider self-avoiding walks on the cubic lattice confined to a half-space by a surface plane ($z = 0$) which we take to be a square lattice. Let c_n^1 be the number of n-step walks which have their first vertex in this plane and c_n^{11} be the corresponding number which also have their last vertex in the plane. Whittington [4] has shown that

$$\lim_{n\to\infty} \frac{1}{n} \ln c_n^1 = \lim_{n\to\infty} \frac{1}{n} \ln c_n^{11} = \kappa. \tag{1.10}$$

It is assumed that a similar n dependence holds for c_n^1 and c_n^{11} so that

$$c_n^1 \sim e^{n\kappa} n^{\gamma_1 - 1}, \quad c_n^{11} \sim e^{n\kappa} n^{\gamma_{11} - 1}. \tag{1.11}$$

In general, for self-avoiding walks analytic treatments have proved to be very difficult. Hence, extensive work has been done to investigate the problem by numerical techniques including series expansion analysis of exact enumeration data, Monte Carlo simulation and transfer matrix methods.

1.1.2 Polymer structures and topologies

Not all polymers are linear. Many parasitic reactions occurring during the synthesis can lead to a chain which is not perfectly linear but contains branch points. In the past, these branch points could only be detected experimentally when the fraction of them in the structure was not too small. However, experimental progress has made it possible to detect one branch point in a polymer and it is also possible to insert to a chain a controlled number of branch points to produce a specific polymer structure (Roovers *et al* [5] [6]). Thus, there has been considerable interest in the behaviour of solutions of branched polymers with finite number of branch points and a specified structure (topology) (Miyake and Freed [7], Wilkinson*et al* [8], Lipson *et al* [9], Saleur [10]).

The topology or structure of a polymer network is specified precisely in terms of the number of branch points and the connectivity which describes how these branch points are connected together. An example of such structure is an f-star polymer formed by joining the first vertex of f linear polymers at a vertex of degree f. Figure 1.1 gives some typical polymer structures. For more complex networks, it is usual to take into account only the number of branch points and neglect the connectivity (Duplantier [11], Duplantier and Saleur [12], Gaunt *et al* [13] [14], Lipson and Whittington [15]). The goal of such models is to predict the effects of branching on the properties of polymers with excluded-volume effect.

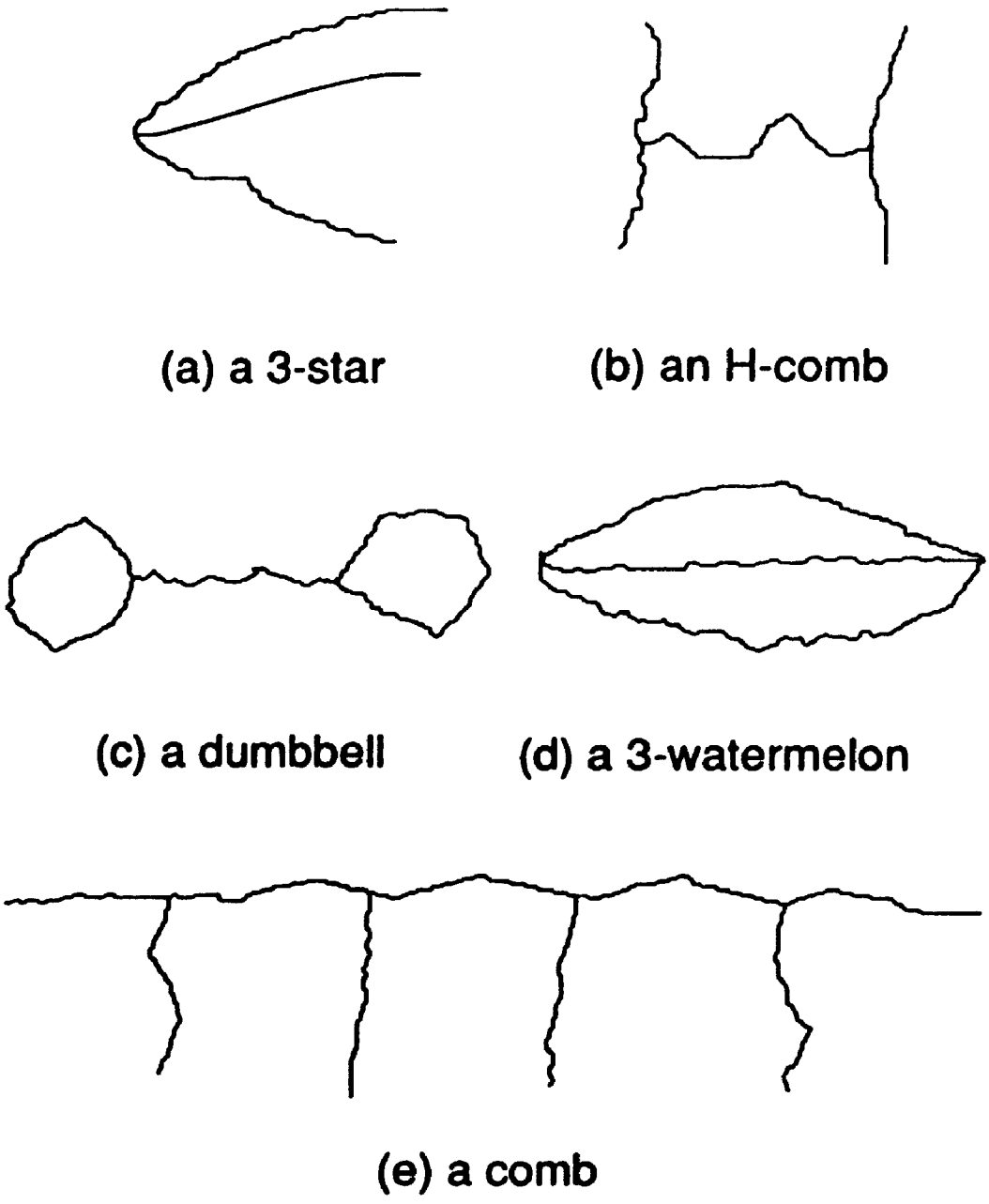


Figure 1.1: Examples of polymer networks

All these networks are modelled as graphs on a lattice. It has been shown that for large n, the number of configurations of a network , g_n, behaves like

$$g_n \sim e^{n\kappa} n^{\gamma_g - 1}, \tag{1.12}$$

where the connective constant κ is the same as that for SAWs, but the exponent γ_g depends on the structure.

1.1.3 Lattice animals

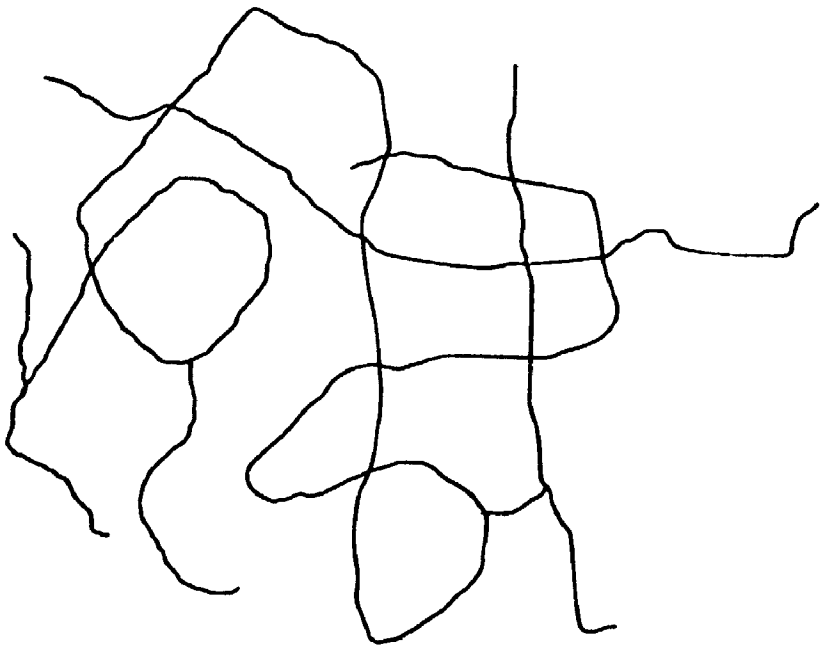


Figure 1.2: A polymer gel

Under proper conditions, branching leads to the formation of an infinite molecule or gel which has an unrestricted number of branch points and a general structure (Figure 1.2). Such polymers are modelled as lattice animals These are connected sub-graphs of the lattice. There are two type of lattice animals. A site animal (strong embedding) is a connected section graph of the lattice (so that if two vertices of the animal are on adjacent lattice sites they must be connected by an edge in the animal). A bond animal (weak embedding) is a connected subgraph of the lattice (so that two

vertices of the animal which are on adjacent lattice sites may or may not be connected by an edge in the animal). In each case, an interesting subset is the corresponding set of animals without cycles, which is referred to as bond trees and site trees.

Of primary interest is the statistics of configurations of lattice animals. We write a_n, A_n, t_n and T_n to be the number of bond animals, site animals, bond trees and site trees with n vertices respectively. It has been shown (Klein [16], Soteros and Whittington [17]) that

$$\begin{aligned}
\lim_{n\to\infty} \frac{1}{n} \ln a_n &= \sup_{n>0} \frac{1}{n} \ln a_n = \ln \lambda < \infty, \\
\lim_{n\to\infty} \frac{1}{n} \ln A_n &= \sup_{n>0} \frac{1}{n} \ln A_n \equiv \ln \Lambda < \infty, \\
\lim_{n\to\infty} \frac{1}{n} \ln t_n &= \sup_{n>0} \frac{1}{n} \ln t_n \equiv= \ln \lambda_0 < \infty, \\
\lim_{n\to\infty} \frac{1}{n} \ln T_n &= \sup_{n>0} \frac{1}{n} \ln T_n \equiv \ln \Lambda_0 < \infty,
\end{aligned} \tag{1.13}$$

where the λ's, etc. are called *growth constants*. These are lattice dependent quantities. Moreover (Soteros and Whittington [17]),

$$\lambda > \lambda_0 > \Lambda > \Lambda_0. \tag{1.14}$$

Rigorous results on the rates of approach to the limits in (1.13) do not exist. Generally, it is expected that

$$\begin{aligned}
a_n &\sim n^{-\theta} \lambda^n, \\
t_n &\sim n^{-\theta_0} \lambda_0^n, \\
A_n &\sim n^{-\Theta} \Lambda^n, \\
T_n &\sim n^{-\Theta_0} \Lambda_0^n,
\end{aligned} \tag{1.15}$$

where the θ's, etc. are called *critical exponents* or simply *exponents*. These quantities are believed to be lattice independent but depend only on the dimension.

From an argument due to Lubensky and Isaacson [18], the universality class for these models is independent of the cycle fugacity, which implies that

$$\theta = \theta_0, \quad \Theta = \Theta_0. \tag{1.16}$$

Furthermore, there are numerical results that indicate that

$$\theta = \theta_0 = \Theta = \Theta_0 \tag{1.17}$$

(Duarte and Ruskin [19], Gaunt [20]).

In order to study the crossover from trees to animals, Whittington *et al* [21] introduced c-animals, which are lattice animals with c (referrd as cyclomatic index) independent cycles. Denoting by $a_n(c)$ and $A_n(c)$ the number of bond c-animals and site c-animals with n vertices respectively, they have shown rigorously that

$$\lim_{n\to\infty} \frac{1}{n} \ln a_n(c) = \ln \lambda_0. \tag{1.18}$$

With the assumption that

$$a_n(c) \sim n^{-\theta_c} \lambda_0^n, \tag{1.19}$$

Soteros and Whittington [22] have shown rigorously that

$$\theta_c = \theta_0 - c \tag{1.20}$$

if either of the exponents exists. For site c-animals, numerical evidence suggests that the growth constant is independent of the cyclomatic index, i.e. $\Lambda_c = \Lambda_0$, and that $\Theta_c = \Theta_0 - c$ (Gaunt *et al* [20], Whittington [21]). However, there are no rigorous arguments to confirm these two results.

1.2 Relation to critical phenomena

The study of the statistics of polymers with excluded-volume effect is also motivated by their correspondence to classical spin models of magnetism. This analogy may

be formulated as a formal equivalence between SAW's and the $N \to 0$ limit of N-component spin model (De Gennes [1]). One of the simplest derivation of such an equivalence is given as follows (Barber *et al* [23]).

Consider a system of N-component spins $\mathbf{s}_i = (s_i^1, s_i^2, \ldots, s_i^N)$ of fixed length $|\mathbf{s}_i| = (\sum_\alpha (s_i^\alpha)^2)^{1/2} = \sqrt{N}$ located on the sites i of a d-dimensional lattice. The Hamiltonian is

$$-\beta H = K \sum_{ij} \mathbf{s}_i \mathbf{s}_j + L \sum_i s_i^1, \tag{1.21}$$

where the first sum runs over all nearest-neighbour spins on the lattice and the second over all sites. $K = J/T$ is the coupling constant. The magnetic field is taken to be in the direction '1' of spin space. Let

$$m(K, L) = \langle s_i^1 \rangle \tag{1.22}$$

be the expectation value of the component of any spin parallel to the magnetic field L, then the zero-field susceptibility is

$$\chi_0(K, N) = \lim_{L \to 0} \frac{\partial m(K, L)}{\partial L} = \sum_j \langle s_i^1 s_j^1 \rangle_0, \tag{1.23}$$

where the subscript indicates that the expectation value is taken with respect to the Hamiltonian (1.21) with $L = 0$. In the limit $N \to 0$, it turns out that

$$\lim_{N \to 0} \chi(K, N) = C(K) = \sum_{n=0}^{\infty} c_n K^n, \qquad c_0 = 1, \tag{1.24}$$

where $C(K)$ is the generating function for n-step walks. From the asymptotic behaviour (1.6), it follows that $C(K)$ has a singularity at $K = K_c = J/T_c = e^{-\kappa}$ of the form

$$C(K) \sim A(1 - e^{\kappa} K)^{-\gamma}, \tag{1.25}$$

analogous to the singularity in the susceptibility. The number of steps n along the walks is inversely proportional to the temperature distance from the critical point, $t = (T/T_c - 1) \propto 1/n$. The bulk correlation length ξ translates into the mean-squared end-to-end distance $\langle R_n^2 \rangle$ of the walks.

To discuss the problem of a self-avoiding walk near an interface, one can consider the same magnetic model on a d-dimensional half-space bounded by a free surface, and allow an additional magnetic field L_1 (again in the '1' direction of spin space) to couple to spins in the surface layer. Let i denote any surface site and define

$$m_1(K, L, L_1) = \langle s_i^1 \rangle. \tag{1.26}$$

Two different surface susceptibilities can be defined (Binder and Hohenberg [24], Barber [25], Binder [26]) by

$$\chi_1(K, N) = \lim_{L \to 0} \frac{\partial m_1(K, L, L_1 = 0)}{\partial L} = \sum_j \langle s_i^1 s_j^1 \rangle_0, \tag{1.27}$$

and

$$\chi_{11}(K, N) = \lim_{L_1 \to 0} \frac{\partial m_1(K, L = 0, L_1)}{\partial L_1} = \sum_j \langle s_i^1 s_j^1 \rangle_0. \tag{1.28}$$

Similarly, in the limit $N \to 0$, one obtains

$$\lim_{N \to 0} \chi_1(K, N) = C_1(K) = \sum_{n \geq 0} c_n^1 K^n, \tag{1.29}$$

and

$$\lim_{N \to 0} \chi_1(K, N) = C_{11}(K) = \sum_{n \geq 0} c_n^{11} K^n, \tag{1.30}$$

where c_n^1 and c_n^{11} are the number of n-step walks given by (1.10). The required indices γ_1 and γ_{11} as defined in (1.11) are now seen, via (1.29) and (1.30), to be analogous to the critical exponents of χ_1 and χ_{11} at the bulk critical temperature K_c. According to the scaling theory in the analogous magnetic problem, γ_1 and γ_{11} are related through

$$2\gamma_1 - \gamma_{11} = \gamma + \nu. \tag{1.31}$$

This has been numerically tested for self-avoiding walks (Barber [23], De'Bell *et al* [27]).

For polymer networks, Ohno and Binder [28] have derived a similar formal equivalence between the generating function for the total number of configurations and the multi-spin correlation function of the N-component spin model in the limit $N \to 0$.

Parisi and Sourlas [29] have shown that the effective Hamiltonian written by Lubensky and Isaacson [18] for lattice animals is equivalent to the effective Hamiltonian for the Ising model in a quenched random external field. They related the critical exponent $\theta(d)$ in d dimensions to the critical exponent $\sigma(d)$ which controls the behaviour of the magnetization near a Lee-Yang singularity in the Ising model in the presence of an imaginary external field in $d-2$ dimensions. That is,

$$\theta(d) = \sigma(d-2) + 2. \tag{1.32}$$

This suggests that for $d = 2$, $\theta = 1$ and for $d = 3$, $\theta = 3/2$. These values are certainly consistent with the available numerical evidence.

Lattice animals are also closely related to percolation clusters although the associated weights are different in the two problems (Broadbent and Hammersley [30], Lubensky and Issacson [18], Kesten [31]).

1.3 The interaction of polymers with a surface

Except for the excluded-volume effect, the polymers considered so far are not subject to any interaction. The problem of these lattice models interacting with a surface (with an energy) has attracted considerable attention since it provides models for the study of polymer adsorption at a surface. Such a study for adsorbed polymers provides tests of our understanding of critical behaviour at a surface. The interaction problem for linear polymers has been studied using both rigorous (Hammersley *et al* [32] and numerical results (e.g, Ishinabe [33] [34] [35]). This problem is also related to the previous $N \to 0$ limit spin model in which the nearest-neighbour interactions between spins are enhanced in the surface. The adsorption transition of polymers then corresponds to the so-called special transition of magnetism (Eisenriegler [36], Binder [26], De'Bell and Lookman [37]).

In this thesis, we will examine a number of polymer models interacting with an

adsorption surface. Of primary interest is the influence of the surface on configuration and adsorption properties. We shall be particularly concerned with models that are discrete and are embedded in the d-dimensional hypercubic lattice in which a vertex is a point in d-dimensional Euclidean space with integer coordinates $\mathbf{x} = (x_1, \ldots, x_d)$. In two dimensions, this is a square lattice and in three dimensions it is a simple cubic lattice. We define the unit vectors $\mathbf{e}_1 = (1, 0, \ldots, 0)$, $\mathbf{e}_2 = (0, 1, \ldots, 0)$, ..., $\mathbf{e}_d = (0, 0, \ldots, 1)$ and the unordered pair $[\mathbf{x}(i), \mathbf{x}(j)]$ as the edge joining the two vertices $\mathbf{x}(i)$, $\mathbf{x}(j)$.

In chapter 2, we consider the adsorption of linear polymers. Some numerical estimates will be presented for the phase transition point and related critical parameters at the point.

In chapter 3, we show rigorously that polymer networks with a specified topology have the same adsorption properties as that for linear polymers. For a special network, named twin-tailed tadpole, we obtain a rigorous result for its critical exponent by relating it to the exponent γ in (1.6) for linear polymers.

In chapter 4, we deal with randomly branched polymers which are modelled as lattice animals. We show the existence of an adsorption (or phase) transition for lattice animals. We also generalize some results from the bulk to the case where an adsorption surface exists. Numerical estimates of the transition points are also given.

In chapter 5, we summarize the basic results of the thesis.

Chapter 2

Self-avoiding walks interacting with a surface

Self-avoiding walks on a d-dimensional lattice and interacting with a $(d-1)$-dimensional surface have been considered as a model for the study of polymer adsorption with a binding energy ω for each monomer attached to the surface (Hammersley *et al* [32]). The two models studied differ according to the type of surface involved. The surface can be impenetrable, in which case the walks are restricted to lie on one side of the surface. This corresponds to the adsorption of polymers at a solid-liquid interface. For a penetrable surface, walks are not confined to lie one side of the surface. Hammersley *et al* [32] have suggested that it may correspond to the adsorption of polymers at a liquid-liquid interface. Aspects of work included in this chapter have previously appeared in Zhao *et al* [38].

2.1 The adsorption of linear polymers

2.1.1 The existence of a phase transition

Let $\mathcal{A}_{n,m}$ be the set of n-step SAWs with $\mathrm{x}(0) = 0$ (i.e. which start at the origin) with exactly $m+1$ vertices in the penetrable surface $x_1 = 0$. Let $\mathcal{A}^+_{n,m}$ be the subset of $\mathcal{A}_{n,m}$ such that $x_1(i) \geq 0$ for all $i = 0, 1, \ldots, n$, which corresponds to $x_1 = 0$ being an impenetrable surface. We denote by $a_{n,m}$ and $a^+_{n,m}$ the number of n-step walks in

$A_{n,m}$ and $A^+_{n,m}$ respectively. We define the partition functions

$$A_n(\omega) = \sum_{m=0}^{n} a_{n,m} e^{m\omega}; \tag{2.1}$$

$$A^+_n(\omega) = \sum_{m=0}^{n} a^+_{n,m} e^{m\omega}. \tag{2.2}$$

Hammersley *et al* [32] have shown that the limits,

$$\lim_{n\to\infty} \frac{1}{n} \ln A_n(\omega) = A(\omega), \tag{2.3}$$

$$\lim_{n\to\infty} \frac{1}{n} \ln A^+_n(\omega) = A^+(\omega), \tag{2.4}$$

hereafter referred to as the *reduced free energies*, exist for all ω. $A(\omega)$ and $A^+(\omega)$ are convex non-decreasing continuous functions of ω and satisfy

$$\max\{\kappa,\ \kappa' + \omega\} \le A^+(\omega) \le A(\omega) \le \max\{\kappa,\ \kappa + \omega\}, \tag{2.5}$$

where κ and κ' are the connective constants of the d and $(d-1)$ dimensional lattices respectively. Moreover, there exists a phase transition point for each case defined by

$$\omega_c = \sup\{\omega :\ A(\omega) = \kappa\}; \tag{2.6}$$

$$\omega^+_c = \sup\{\omega :\ A^+(\omega) = \kappa\}. \tag{2.7}$$

Physically, these results imply the existence of the ordinary, adsorption and surface transition for linear polymers modelled by SAWs (Binder [26]). For $\omega < \omega_c$ ($\omega < \omega^+_c$), the connective constant for a polymer attached to the surface retains the value for a polymer in the bulk solution. For $\omega > \omega_c$ ($\omega > \omega^+_c$), the connective constant decreases and approaches a limit given by the connective constant for the corresponding $(d-1)$ dimensional bulk problem (which will be shown rigorously later). The value of ω_c (ω^+_c) then corresponds to the critical value of the attractive interaction of the monomers with the surface at which the surface adsorption transition occurs.

At the transition points, two crossover exponents ϕ and ϕ^+ are defined by

$$A(\omega) - A(\omega_c) \sim (\omega - \omega_c)^{1/\phi}, \quad \omega > \omega_c, \tag{2.8}$$

$$A^+(\omega) - A^+(\omega_c^+) \sim (\omega - \omega_c^+)^{1/\phi^+}, \quad \omega > \omega_c^+, \tag{2.9}$$

which describe the variation of $A(\omega)$ and $A^+(\omega)$ with ω at the transition points ω_c and ω_c^+ respectively. From (2.1), (2.5) and (2.6), we have that, as $\omega - \omega_c \to 0^+$,

$$A_n(\omega) = \sum_{m=0}^{n} a_{n,m} e^{m\omega_c} e^{m(\omega-\omega_c)} \leq A_n(\omega_c) e^{n(\omega-\omega_c)}, \tag{2.10}$$

and then

$$A(\omega) \leq A(\omega_c) + (\omega - \omega_c), \tag{2.11}$$

or

$$A(\omega) - A(\omega_c) \leq (\omega - \omega_c). \tag{2.12}$$

Combining (2.12) with (2.8) and the continuity of $A(\omega)$ at ω_c gives

$$0 \leq \phi \leq 1. \tag{2.13}$$

Similarly, one can have

$$0 \leq \phi^+ \leq 1. \tag{2.14}$$

Similarly, one can also define the corresponding partition functions for SAW's with number of edges in the surfaces. The above corresponding results can also be derived.

2.1.2 The scaling form at the phase transition point

Analogous to (1.6), it is assumed that

$$A_n(\omega) \sim e^{nA(\omega)} n^{\gamma(\omega)-1}; \tag{2.15}$$

$$A_n^+(\omega) \sim e^{nA^+(\omega)} n^{\gamma^+(\omega)-1}. \tag{2.16}$$

Renormalization group arguments (Kremer [39], Diehl [40]) indicate that there is a single value of $\gamma^+(\omega)$ for each of the transitions discussed above as follows

$$\gamma^+(\omega) = \gamma_1, \quad \omega < \omega_c^+, \tag{2.17}$$

$$\gamma^+(\omega) = \gamma_1^{ad}, \quad \omega = \omega_c^+, \tag{2.18}$$

$$\gamma^+(\omega) = \gamma_1^s, \quad \omega > \omega_c^+. \tag{2.19}$$

Moreover these arguments show that γ_1^s is equal to the value of γ for $(d-1)$-dimensional system.

The generating functions of the partition functions are defined by

$$G(x,y) = G(x,\omega) = \sum_{m\le n} a_{n,m} e^{m\omega} x^n = \sum_{m\le n} a_{n,m} y^m x^{n-m}, \tag{2.20}$$

$$G^+(x,y) = G^+(x,\omega) = \sum_{m\le n} a^+_{n,m} e^{m\omega} x^n = \sum_{m\le n} a^+_{n,m} y^m x^{n-m} \tag{2.21}$$

with $e^\omega = y/x$.

From (2.15), the generating function G has singularities at $x_c = e^{-A(\omega)}$ of the form

$$G(x,y) = G(x,\omega) \sim [x_c(\omega) - x]^{-\gamma(\omega)}. \tag{2.22}$$

The trajectory of the singularities in the xy plane is represented in terms of the parameter ω by

$$x_c(\omega) = e^{-A(\omega)}, \quad y_c(\omega) = e^{\omega - A(\omega)}. \tag{2.23}$$

From the property of $A(\omega)$, one can show the following:

(a) For $\omega \le \omega_c$, the trajectory is a vertical line corresponding to $x_c(\omega) \equiv e^{-\kappa}$. As ω crosses ω_c, $x_c(\omega)$ begins to decrease. The adsorption transition point is

$$x_c = x_c(\omega_c) = e^{-\kappa}, \quad y_c = y_c(\omega_c) = e^{\omega_c - \kappa}. \tag{2.24}$$

(b) Near the adsorption transition point, from (2.8) and (2.23), we have that as $\omega - \omega_c \to 0^+$,

$$\begin{aligned} y - y_c &= (e^\omega - e^{\omega_c})x + (x - x_c)e^{\omega_c} \\ &\sim x_c e^{\omega_c}(x_c - x)^\phi + e^{\omega_c}(x - x_c) \\ &\sim (x_c - x)^\phi. \end{aligned} \tag{2.25}$$

(c) As $\omega \to \infty$, from equation (2.29) given in section 2.1.3, we have

$$x_c(\omega) = e^{-A(\omega)} \to 0, \quad y_c(\omega) = e^{\omega - A(\omega)} \to e^{-\kappa'}. \tag{2.26}$$

Hence (2.23) gives the phase boundary represented in Figure 2.1 which has been previous described (Nakanishi [41], De'Bell and Essam [42]). The same arguments also apply to $G^{+}(x, y)$.

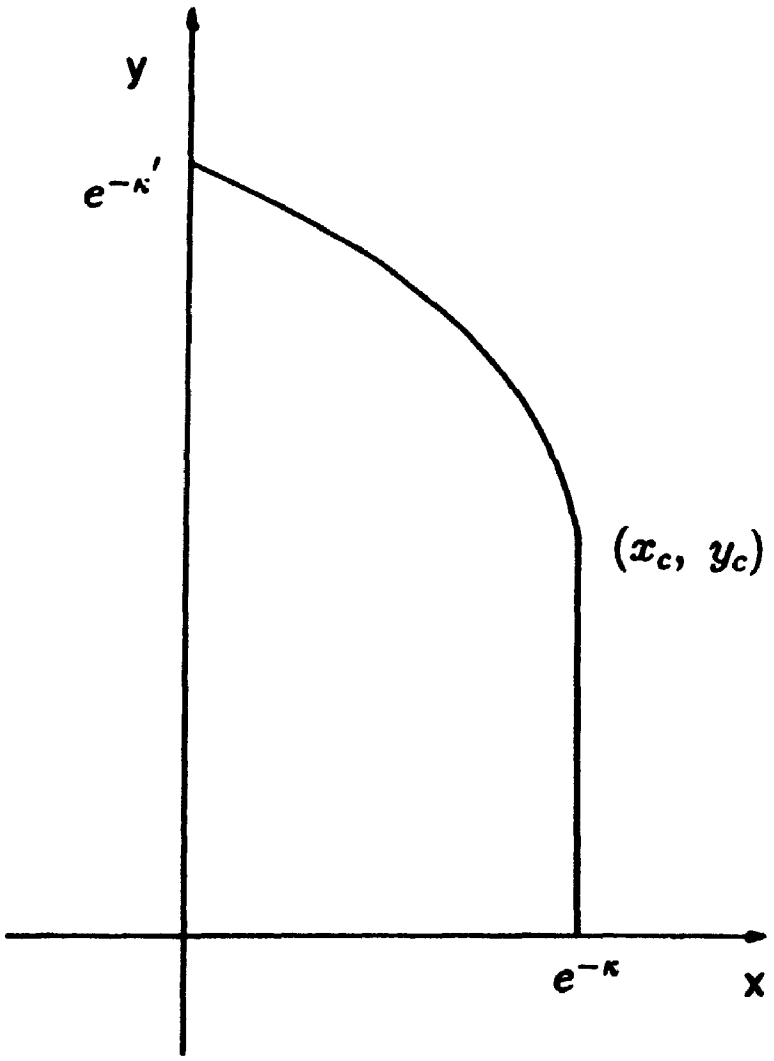


Figure 2.1: Schematic phase boundary given by (a)-(c).

There are arguments analogous to those given in section 1.2 that show that the two generating functions for SAW's with number of edges in the surfaces correspond to the expansion of the high-temperature susceptibility for an N-component spin system with a defect plane and N-component semi-infinite system in the limit $N \to 0$ respectively (Nakanishi [41], Ishinabe [35], Binder [26], De'Bell and Lookman [37]). The fugacity x is the interaction parameter K in the bulk and y corresponds to the interaction parameter K_1 in the surface. From the scaling theory, the generating function G^+ is assumed to be a generalized homogeneous function near the adsorption transition in terms of $e^{\omega} - e^{\omega_c}$ and $x_c - x$ and has the scaling form

$$G(\omega, x) \sim (x_c - x)^{-\gamma^{sd}} Z((e^{\omega} - e^{\omega_c})/(x_c - x)^{\phi^+}). \tag{2.27}$$

(Binder [26]). From (2.25), the scaling form can then be written, in terms of x and y, as

$$G^+(x, y) = (x - x_c)^{-\gamma^{sd}} Z\left(\frac{(y - y_c) + e^{\omega_c^+}(x_c - x)}{(x_c - x)^{\phi^+}}\right). \tag{2.28}$$

By analogy, one may assume the same scaling form for $G(x, y)$ at its special transition point.

2.1.3 The asymptotic behaviour of $A^+(\omega)$ and $A(\omega)$ as $\omega \to \infty$

In section 2.1.1, we have mentioned that for $\omega > \omega_c$ ($\omega > \omega_c^+$), the connective constant decreases and has a limit given by the connective constant for the corresponding $(d-1)$-dimesional bulk problem. This corresponds to showing that

$$\lim_{\omega \to \infty} [A^+(\omega) - \omega] = \lim_{\omega \to \infty} [A(\omega) - \omega] = \kappa'. \tag{2.29}$$

The result is derived by considering the interaction between the adsorption surface and linear polymers referred to as nonuniform 2-stars defined below.

Nonuniform 2-star

A nonuniform 2-star is an n-step SAW which has one of its vertices at the origin **0**. Such a vertex is termed the "branch point" of the 2-star. The segment from the branch point to one of the two vertices $\mathbf{x}(0)$ and $\mathbf{x}(n)$ is referred to as one "branch" of the nonuniform 2-star. It is an n_i-step SAW ($n_i \geq 0$) with $n_1 + n_2 = n$. The term "nonuniform" indicates that n_1 may not equal to n_2. From such a definition, a SAW with $\mathbf{x}(0) = \mathbf{0}$ is a special case of a nonuniform 2-star with only one branch. By analogy, the partition functions are defined as

$$S_n(2,\omega) = \sum_{m=0}^{n} s_{n,m}(2)e^{m\omega}, \tag{2.30}$$

$$S_n^+(2,\omega) = \sum_{m=0}^{n} s_{n,m}^+(2)e^{m\omega}, \tag{2.31}$$

where $s_{n,m}(2)$ and $s_{n,m}^+(2)$ are the number of n-step 2-stars with $m+1$ vertices in the penetrable surface and the impenetrable surface respectively.

Lemma 2.1 *For any* ω,

$$\lim_{n\to\infty} \frac{1}{n} \ln S_n(2,\omega) = A(\omega); \tag{2.32}$$

$$\lim_{n\to\infty} \frac{1}{n} \ln S_n^+(2,\omega) = A^+(\omega). \tag{2.33}$$

Proof: The proof is the same for both limits, so we deal with (2.32). Since a SAW starting at **0** is a special case of a nonuniform 2-star with only branch, we obtain

$$A_n(\omega) \leq S_n(2,\omega). \tag{2.34}$$

Consider a subset $\mathcal{C}_n$ of $\mathcal{A}_n$ that satisfies the conditions:

$$0 = x_1(0) = x_1(n), \tag{2.35}$$

and

$$0 = x_d(0) \leq x_d(i) < x_d(n), \qquad i = 1, \ldots, n-1. \tag{2.36}$$

The partition function for such walks is defined as

$$C_n(\omega) = \sum_{m=0}^{n} c_{n,m} e^{m\omega}. \tag{2.37}$$

It has been shown (Hammersley *et al* [32]) that

$$C_n(\omega)C_{n'}(\omega) \le (n+n'+1)C_{n+n'}(\omega), \tag{2.38}$$

and

$$C_n(\omega) \le A_n(\omega) \le (2n+5)^{d+1/2} e^{c\sqrt{n}+2|\omega|} C^{1/2}_{2n+4}(\omega), \tag{2.39}$$

which implies that

$$\lim_{n\to\infty} \frac{1}{n} \ln C_n(\omega) = A(\omega). \tag{2.40}$$

By treating each branch of a 2-star independently, we obtain

$$S_n(2,\omega) \le \sum_{n_1+n_2=n} A_{n_1}(\omega) A_{n_2}(\omega) \tag{2.41}$$

From (2.38) and (2.39), equation (2.41) is replaced by

$$\begin{aligned} S_n(2,\omega) &\le \sum_{n_1+n_2=n} (2n_1+5)^{d+1/2} e^{c\sqrt{n_1}+2|\omega|} C^{1/2}_{2n_1+4}(\omega) \\ &\quad \cdot (2n_2+5)^{d+1/2} e^{c\sqrt{n_2}|\omega|} C^{1/2}_{2n_2+4}(\omega) \\ &\le (n+1)(2n+9)(2n+5)^{2d+1} e^{c'\sqrt{n}+4|\omega|} C^{1/2}_{2n+8}(\omega). \end{aligned} \tag{2.42}$$

Combining it with (2.34) and (2.40), we obtain

$$\lim_{n\to\infty} \frac{1}{n} \ln S_n(2,\omega) = A(\omega). \tag{2.43}$$

The establishment of (2.29)

Lemma 2.2 *For $\omega \ge 0$ and any n,*

$$A(\omega) \le \frac{1}{n} \ln S_n(2,\omega), \tag{2.44}$$

where $S_n(2,\omega)$ is given in (2.30).

Proof: By translation, any n-step SAW in the bulk can be mapped to at least one nonuniform 2-star, which is totally confined to one side of the surface. This mapping is injective. Hence we have

$$a_n \leq S_n(2,0). \tag{2.45}$$

Consider an $(n_1 + n_2)$-step SAW with $\mathbf{x}(0) = \mathbf{0}$ and a total $(i+1)$ vertices in the adsorption surface. By cutting it at the vertex $\mathbf{x}(n_1)$, we obtain two SAWs. By translating until both of them have some vertices in the surface, we obtain two nonuniform 2-stars with a total $(i'+1) \geq (i+1)$ vertices in the surface. Since not all two 2-stars can be obtained in this way, we have, for $\omega \geq 0$ $(e^{\omega} \geq 1)$:

$$S_{n_1}(2,\omega)S_{n_2}(2,\omega) \geq A_{n_1+n_2}(\omega). \tag{2.46}$$

For an integer n and fixed integer m, one can write $n = qm+r$ with $0 \leq r < m-1$. By repeating the inequality (2.46), one obtains

$$A_n(\omega) \leq S_m(2,\omega)^q S_r(2,\omega), \tag{2.47}$$

or

$$\frac{1}{n}\ln A(\omega) \leq \frac{qm}{n}\cdot\frac{1}{m}\ln S_m(2,\omega) + \frac{1}{n}\ln S_r(2,\omega). \tag{2.48}$$

Letting $n \to \infty$ then yields

$$A(\omega) \leq \frac{1}{m}\ln S_m(2,\omega). \tag{2.49}$$

Replacing m by n gives (2.44). The analogous inequality between $A^+(\omega)$ and $S_n^+(2,\omega)$ can also be obtained by following the same arguments.

Theorem 2.1 *As $\omega \to \infty$, the limits*

$$\lim_{\omega\to\infty}[A^+(\omega) - \omega] = \lim_{\omega\to\infty}[A(\omega) - \omega] = \kappa' \tag{2.50}$$

exist.

Proof: From (2.5) and (2.44), we obtain

$$\kappa' \leq A^+(\omega) - \omega \leq A(\omega) - \omega \leq \frac{1}{n} \ln S_n(2,\omega) e^{-n\omega}. \tag{2.51}$$

Let $\omega \to \infty$, we obtain

$$\begin{aligned} \kappa' &\leq \lim_{\omega\to\infty} [A^+(\omega) - \omega] \leq \lim_{\omega\to\infty} [A(\omega) - \omega] \\ &\leq \lim_{\omega\to\infty} \frac{1}{n} \ln S_n(2,\omega) e^{-n\omega} = \frac{1}{n} \ln s_{n,n}(2), \end{aligned} \tag{2.52}$$

where $s_{n,n}(2)$ is the number of 2-stars embedded in the corresponding $(d-1)$-dimen -sional lattice. From (2.43), we obtain

$$\lim_{n\to\infty} \frac{1}{n} \ln s_{n,n}(2) = \kappa'. \tag{2.53}$$

Substituting it in (2.52) yields

$$\lim_{\omega\to\infty} [A^+(\omega) - \omega] = \lim_{\omega\to\infty} [A(\omega) - \omega] = \kappa'. \tag{2.54}$$

2.2 Numerical analysis of the critical parameters near the transition point

In section 2.1, we have discussed the interaction of self-avoiding walks with either a penetrable or an impenetrable surface. For each model, a phase transition exists and at which a crossover exponent ϕ is defined. These two exponents are believed to take different values. For impenetrable surfaces, numerical results indicate that $\phi = 0.5(d = 2)$ (Ishinabe [33], Guim and Burkhardt [43], Burkhardt *et al* [44]) and $\phi = 0.59(d = 3)$ (Eisenriegler *et al* [36]). For penetrable surfaces, scaling theory predicts $\phi = 1 - \nu$ (Bray and Moore [45]). From the generally accepted numerical value of $\nu = 0.75(d = 2)$ and $\nu = 0.59(d = 3)$, we obtain that $\phi = 0.25(d = 2)$ and

$\phi = 0.41(d = 3)$. However, the series analysis of Ishinabe [35] yields an estimate of $\phi = 0.5$ for $d = 2$ and $\phi = 0.59$ for $d = 3$, inconsistent with the scaling prediction. His analysis seems to suggest that the two models have the same crossover behavior at their own respective transition points for $d = 2$ and $d = 3$.

In this section, we test Ishinabe'e results by analyzing the available two variable series for SAW's for the penetrable and impenetrable problems on a number of lattices in two and three dimensions. The method we use is partial differential approximants (PDA) introduced by Fisher [46], which has been previously applied to spin system (Stilck and Salinas [47]). The series for the penetrable surface are also analysed by using a one variable analysis.

2.2.1 Partial differential approximants

The method of partial differential approximants (PDA) is a generalization of $d$log Padé approximants for a function $f(x, y)$ of two variables with a truncated expansion around the origin. The assumed scaling form for the function near its critical point $(x_c,\ y_c)$ is

$$f(x,y) \sim \mid \Delta\tilde{x} \mid^{-\gamma} Z(\Delta\tilde{y}/ \mid \Delta\tilde{x} \mid^{\phi}), \tag{2.55}$$

where ϕ is the crossover exponent. The parameters in this expression are given by

$$\Delta\tilde{x} = \Delta x - (1/e_2)\Delta y, \qquad \Delta\tilde{y} = \Delta y - e_1\Delta x, \tag{2.56}$$

where

$$\Delta x = x_c - x, \qquad \Delta y = y_c - y, \tag{2.57}$$

and e_1 and e_2 are two scaling parameters to specify the derivative of x and y near the critical point.

By differentiating $f(x, y)$ with x and y respectively, we obtain

$$f_x(x,y) = (\gamma/\Delta\tilde{x})f(x,y) + \mid \Delta\tilde{x} \mid^{-(\gamma+\phi)} Z'(\Delta\tilde{y}/ \mid \Delta\tilde{x} \mid^{\phi})[e_1 + \phi(\Delta\tilde{y}/\Delta\tilde{x})], \tag{2.58}$$

and

$$f_y(x,y) = -(\gamma/e_2\Delta\tilde{x})f(x,y) - \mid \Delta\tilde{x} \mid^{-(\gamma+\phi)} Z'(\Delta\tilde{y}/\mid \Delta\tilde{x} \mid^{\phi})[1 + (\phi/e_2)(\Delta\tilde{y}/\Delta\tilde{x})]. \tag{2.59}$$

By multiplying the first equation by $[\Delta\tilde{x} + (\phi/e_2)\Delta\tilde{y}]$ and the second equation by $(e_1\Delta\tilde{x} + \phi\Delta\tilde{y})$ and adding them together, we obtain

$$\begin{aligned} & [\Delta\tilde{x} + (\phi/e_2)\Delta\tilde{y}]f_x(x,y) + (e_1\Delta\tilde{x} + \phi\Delta\tilde{y})f_y(x,y) \\ = \;& \gamma(1 - e_1/e_2)f(x,y). \end{aligned} \tag{2.60}$$

By using expression (2.56), this can be written as

$$\begin{aligned} & \{[1 - \phi\frac{e_1}{e_2}]\Delta x - (\frac{1}{e_2})(1-\phi)\Delta y\}f_x(x,y) + \{(e_1(1-\phi)\Delta x - (\frac{e_1}{e_2} - \phi)\Delta y\}f_y(x,y) \\ = \;& \gamma(1 - \frac{e_1}{e_2})f(x,y). \end{aligned} \tag{2.61}$$

A partial differential approximant $F_{LMN}(x,y)$ to such a function $f(x,y)$ is a solution of the linear partial differential equation:

$$Q_M(x,y)\frac{\partial F(x,y)}{\partial x} + R_N(x,y)\frac{\partial F(x,y)}{\partial y} = P_L(x,y)F(x,y), \tag{2.62}$$

where

$$\begin{aligned} P_L(x,y) &= \sum_{i,j} p_{ij}x^i y^j, \\ Q_M(x,y) &= \sum_{i,j} q_{ij}x^i y^j, \\ R_N(x,y) &= \sum_{i,j} r_{ij}x^i y^j \end{aligned} \tag{2.63}$$

are polynomials with L, M and N terms respectively and are chosen such that the series solution of $F(x,y)$ in powers of x and y agrees with the known expansion of $f(x,y)$ to some predetermined order.

The critical point $(x_c,\ y_c)$ is estimated by the solution of the set of coupled equations

$$Q_M(x,y) = 0, \quad R_N(x,y) = 0. \tag{2.64}$$

Near this point the polynomials are approximated to the lowest order by

$$\begin{aligned} P_L(x,y) &\approx P_L(x_c,y_c) = P_c, \\ Q_M(x,y) &\approx \frac{\partial Q_M}{\partial x}(x_c,y_c)\Delta x + \frac{\partial Q_M}{\partial y}(x_c,y_c)\Delta y = Q_1\Delta x + Q_2\Delta y, \\ R_N(x,y) &\approx \frac{\partial R_N}{\partial x}(x_c,y_c)\Delta x + \frac{\partial R_N}{\partial y}(x_c,y_c)\Delta y = R_1\Delta x + R_2\Delta y. \end{aligned} \tag{2.65}$$

One thus has in the vicinity of $(x_c,\ y_c)$

$$(Q_1\Delta x + Q_2\Delta y)F_x(x,y) + (R_1\Delta x + R_2\Delta y)F_y(x,y) = P_cF(x,y). \tag{2.66}$$

Identifying it with (2.61) results in the set of relations

$$\begin{aligned} CQ_1 &= 1-\phi(e_1/e_2), \\ CQ_2 &= -(1/e_2)(1-\phi), \\ CR_1 &= e_1(1-\phi), \\ CR_2 &= -e_1/e_2+\phi, \\ CP_c &= \gamma(1-e_1/e_2), \end{aligned} \tag{2.67}$$

where C is a constant. By solving this set of equations, one obtains the formulae

$$e_1,\ e_2 = \frac{1}{2}\frac{R_2-Q_1}{Q_2} \pm \frac{1}{2}\left[\left(\frac{R_2-Q_1}{Q_2}\right)^2 - \frac{4R_1}{Q_2}\right]^{1/2}, \tag{2.68}$$

$$\gamma = -\frac{P_c}{e_2Q_2-R_2}, \tag{2.69}$$

$$\phi = \frac{\gamma(Q_1+R_2)}{P_c} - 1. \tag{2.70}$$

2.2.2 Numerical results

The analysis we report is for bond and site data for $a_{n,m}$ on the square and simple cubic lattices and bond data on the triangular lattice. The data for these lattices are given in references [32]–[34] and [38]. Generally, the results for site data on all

lattices are worse for both the penetrable and impenetrable models. From (2.28), we have that

$$G(x,y) \sim (x_c - x)^{-\gamma} Z\left(\frac{(y-y_c) + e^{\omega_c}(x_c - x)}{(x_c - x)^{\phi}}\right). \tag{2.71}$$

By the exponent γ in (2.71), we mean its value at the adsorption transition (γ^{ad}). Hereafter, in the rest of this chapter, we refer to γ^{ad} as γ. Comparing (2.71) with the generalized form (2.55), we have

$$e_1 = e^{\omega_c}, \qquad e_2 = \infty. \tag{2.72}$$

A PDA depends on three labelling sets which define the polynomials $P_L(x,y)$, $Q_M(x,y)$ and $R_N(x,y)$ and a matching set which is a subset of the labelling set of $F(x,y)$ specifying the powers of x and y of $F(x,y)$ that are to be matched. For convenience, we construct the approximants in two ways: (1) we let the three labelling sets have full triangular forms with $M = N = L$. The matching set of $F(x,y)$ is then selected to be as symmetrical as possible with the main diagonal of the labelling set of $F(x,y)$. (2) we choose a full triangular subset as the matching set and if the number of entries is J, we let $M = N$ and choose L such that $M + N + L = J + 1$. The entries for the polynomials are then chosen to be as close to the triangular form as possible.

In all of our approximants, we find that $| e_2 | \gg 1$ while e_1 varies in a rather large interval and depends on the estimate of $(x_c,\ y_c)$. The estimates of y_c, y_c/x_c, γ and ϕ are given in Table 2.1. Figure 2.2–2.9 are representative plots of y_c versus x_c, γ versus ϕ and γ versus y_c for a number of lattices for bond (or site) data as examples from which the estimates in Table 2.1 are obtained. The estimates for y_c as a function of x_c for all lattices lie on a curve resembling the critical phase diagram (see Figure 2.1 and Figure 2.2–2.4). They do not converge to any particular value, as in a one variable analysis. For values of y less than some value y_c, the approximants concentrate around the bulk value for x_c. The point at which x begins to decrease is taken as the critical point $(x_c,\ y_c)$. The linear correlation seen in the graphs of ϕ versus γ (Figure 2.5–2.7)

is what would be expected if $G(x,y)$ is a generalized homogeneous function in the vicinity of $(x_c,\ y_c)$ (section 2.1.2). The values of ϕ in Table 2.1 are read from a plot of the estimates of ϕ against the estimates of γ by assuming $\gamma(d=2) = 93/64$ (Guim and Burkhardt [43]) and $\gamma(d=3) = 1.44$ (Eisenriegler *et al* [36]) for an impenetrable surface and $\gamma(d=2) = 43/32$ and $\gamma(d=3) = 1.162$ (Gutterman [48]) for a penetrable surface. Correlations of ϕ with x_c and y_c are consistent with these values.

Table 2.1: The estimates of the critical parameters obtained by using partial differential approximants.

Variable	Bond (SQ)	Site (SQ)	Bond (T)	Bond (SC)	Site (SC)
		(a) Impenetrable surface			
x_c	0.37905	0.37905	0.24092	0.2135	
y_c	0.780 ± 0.050	0.690 ± 0.010	0.688 ± 0.015	0.314 ± 0.040	
y_c/x_c	2.060 ± 0.10	1.820 ± 0.030	2.850 ± 0.070	1.470 ± 0.020	
γ	1.450 ± 0.050	1.400 ± 0.050	1.400 ± 0.100	1.550 ± 0.150	
$\phi(x_c)$	$0.500^{+0.000}_{-0.000}$	0.520 ± 0.020	$0.500^{+0.000}_{-0.070}$		
$\phi(y_c)$	$0.500^{+0.100}_{-0.000}$		0.450 ± 0.050		
$\phi(\gamma)$	0.500 ± 0.090	0.520 ± 0.030	0.500 ± 0.010	0.540 ± 0.070	
		(b) Penetrable surface			
x_c	0.37905	0.37905	0.24092	0.2135	0.2135
y_c	0.380 ± 0.010	0.400 ± 0.020	0.250 ± 0.010	0.200 ± 0.020	0.225 ± 0.150
y_c/x_c	1.000 ± 0.020	1.050 ± 0.050	1.030 ± 0.050	0.940 ± 0.080	1.050 ± 0.050
γ	$1.350^{+0.000}_{-0.100}$	$1.350^{+0.000}_{-0.100}$	1.340 ± 0.040	$1.200^{+0.110}_{-0.000}$	1.210 ± 0.030
$\phi(x_c)$	0.260 ± 0.060		0.400 ± 0.200	0.400 ± 0.010	0.580 ± 0.090
$\phi(y_c)$	0.250 ± 0.030	0.260 ± 0.060		0.420 ± 0.020	
$\phi(\gamma)$	0.270 ± 0.040	0.350 ± 0.100	0.350 ± 0.150	0.450 ± 0.090	0.450 ± 0.100

For the impenetrable surface, our result of $\phi = 0.5 \pm 0.04$ in two dimensions is consistent with a value of $\phi = 0.5$, obtained previously from transfer matrix (Guim and Burkhardt [43]), conformal invariance theory (Burkhardt *et al* [44]) and one variable exact enumeration work (Ishinabe [34]) on the square lattice. The va' of γ (Figure 2.5-2.7) is consistent with the result 93/64 given by Guim and Burkhard' 43]. The estimate of 2.05 ± 0.01 for the ratio y_c/x_c agrees with Ishinabe's result for the square lattice bond problem [34] and the estimate 1.80 ± 0.02 agrees with the estimate of Hammersley *et al* for the site data [32]. In three dimensions, $\phi = 0.54 \pm 0.07$ for the

simple cubic lattice is in accord with Monte Carlo results of $\phi = 0.59$ (Eisenriegler *et al* [36]) and our estimate of 1.46 ± 0.01 for y_c/x_c agrees with 1.45 from Monte Carlo work (Ma *et al* [49]) and the estimate 1.50 by considering the zeros of the partition function (Ishinabe [33]).

For the penetrable surface, our estimate of $\phi = 0.28 \pm 0.05$ in two dimensions is not consistent with Ishinabe's result ($\phi = 0.5$) [35], but is in accord with scaling prediction ($\phi = 0.25$). Our value $\phi = 0.40 \pm 0.01$ for the simple cubic is consistent with scaling prediction ($\phi = 0.41$), but does not agree with Ishinabe's result ($\phi = 0.6$) [35].

For the simple cubic lattice, most of the approximants are either poorly conditioned or give good estimates for $(x_c,\ y_c)$, however, because the argument under the square root sign in (2.68) is negative, it is difficult to calculate all critical parameters.

Partial differential approximants are useful in representing critical properties such as the critical line in a plane and the linear correlation of γ and ϕ near the special point. However, since an approximant depends on both the degree and form of the defining polynomials, convergence as that obtained in a one variable analysis is not easy to detect and accurate estimates are difficult.

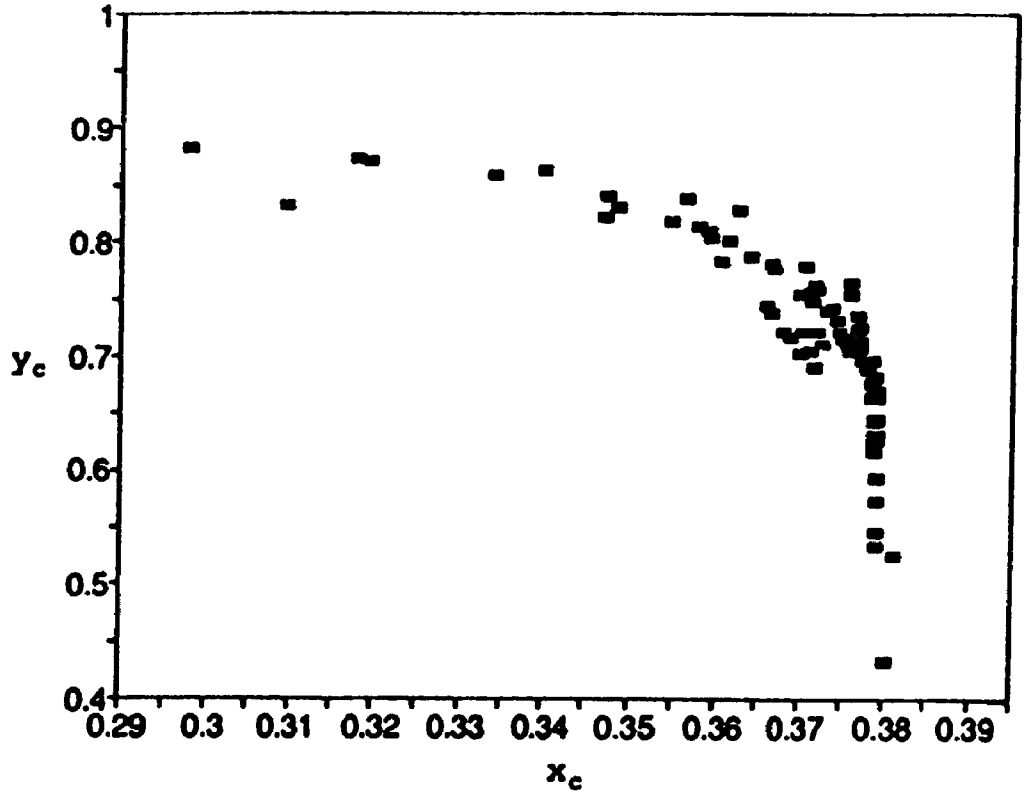


Figure 2.2: Plots of y_c against x_c for square lattice (site) with an impenetrable surface.

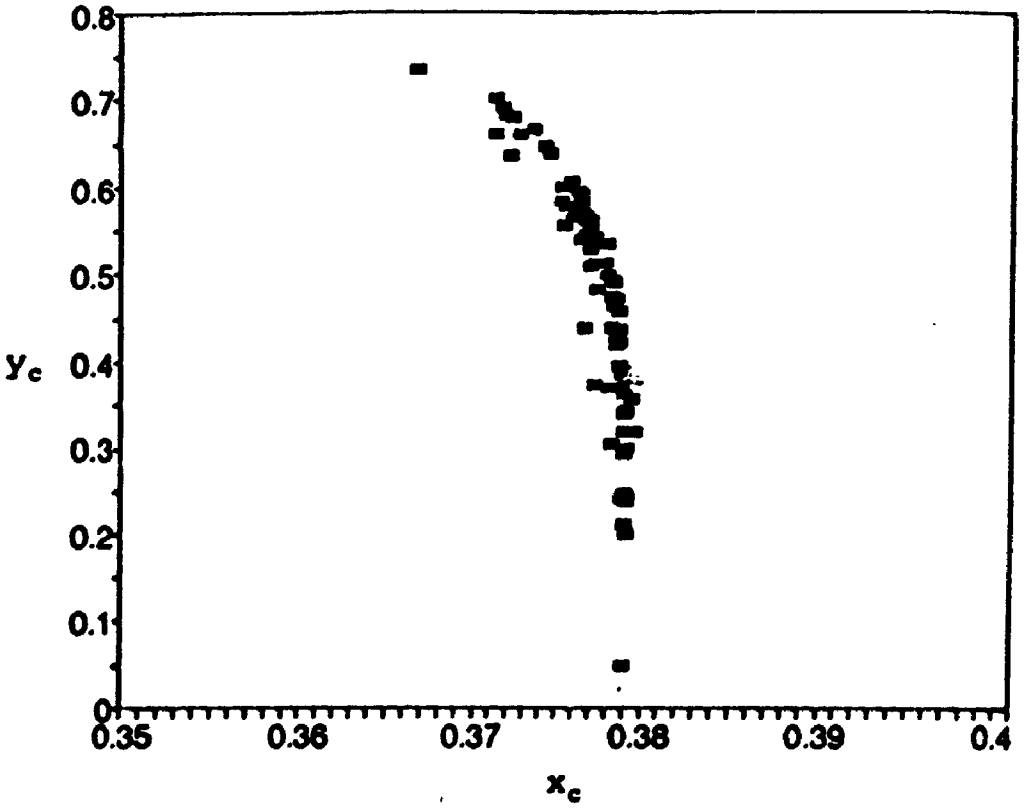


Figure 2.3: Plots of y_c against x_c for square lattice (bond) with a penetrable surface.

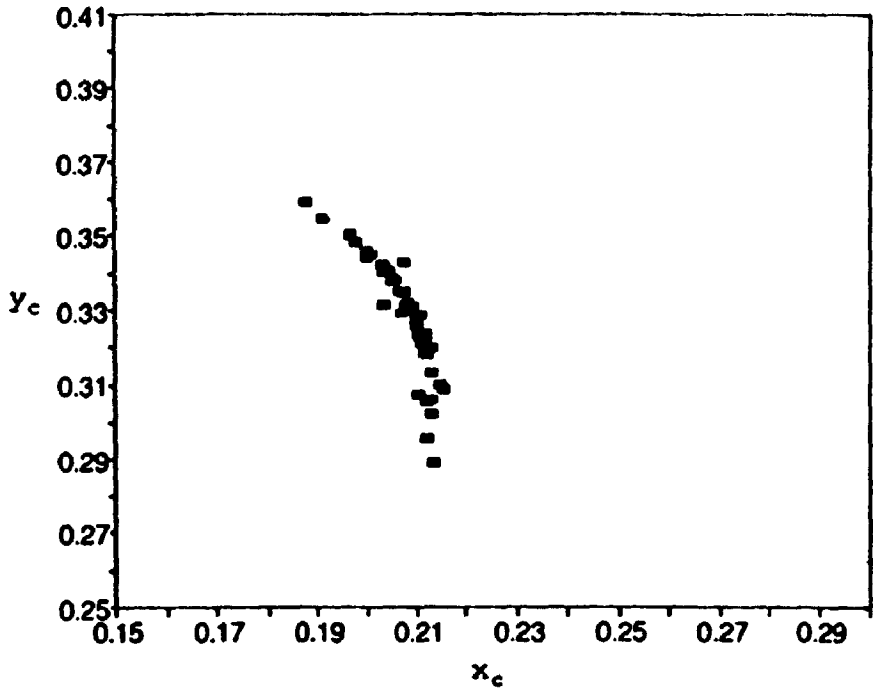


Figure 2.4: Plots of y_c against x_c for simple cubic lattice (bond) with an impenetrable surface.

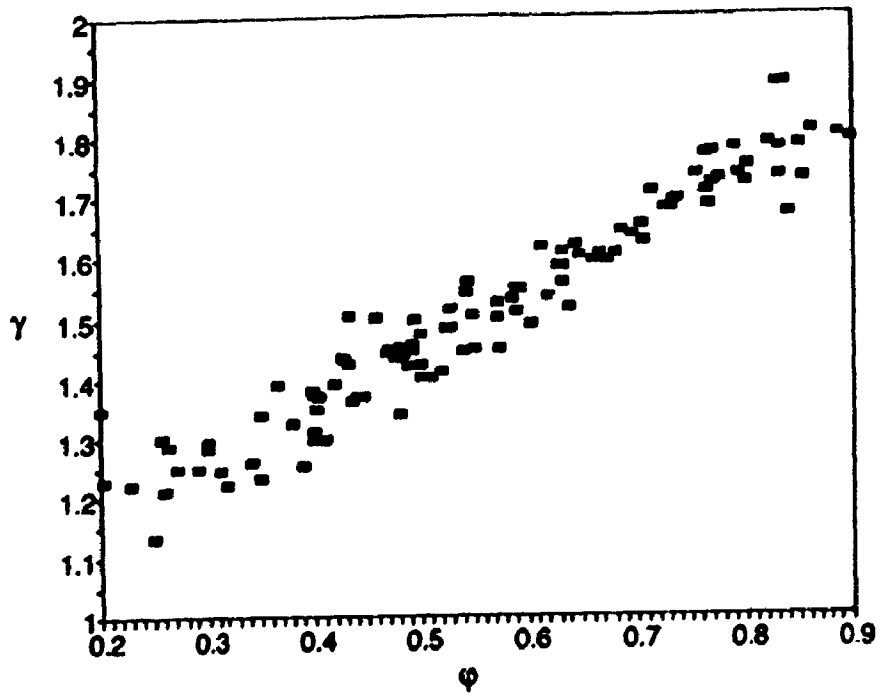


Figure 2.5: The exponent γ is plotted against the crossover exponent ϕ for square lattice (bond) with an impenetrable surface.

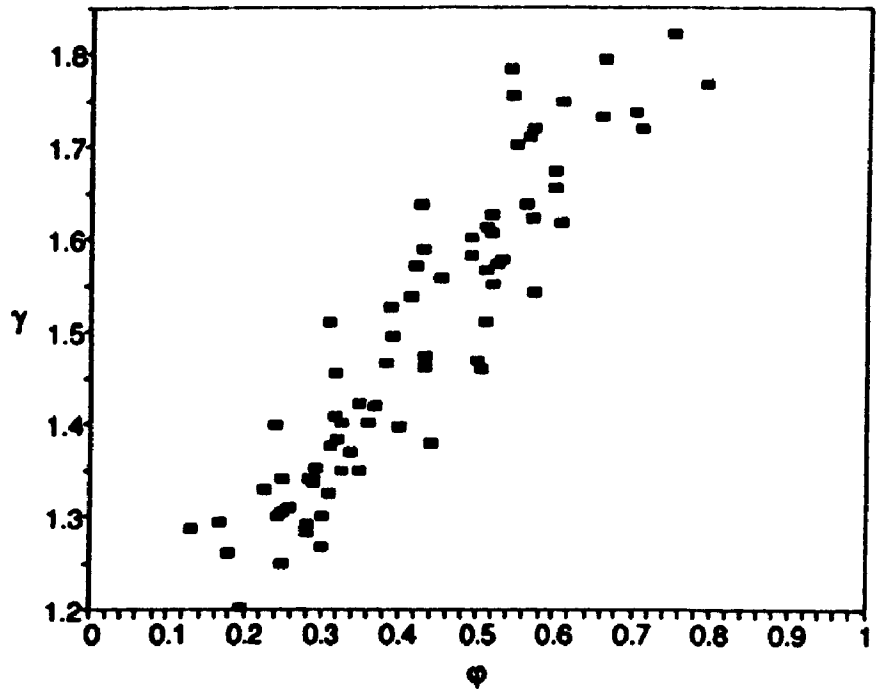


Figure 2.6: The exponent γ is plotted against the crossover exponent ϕ for square lattice (bond) with a penetrable surface.

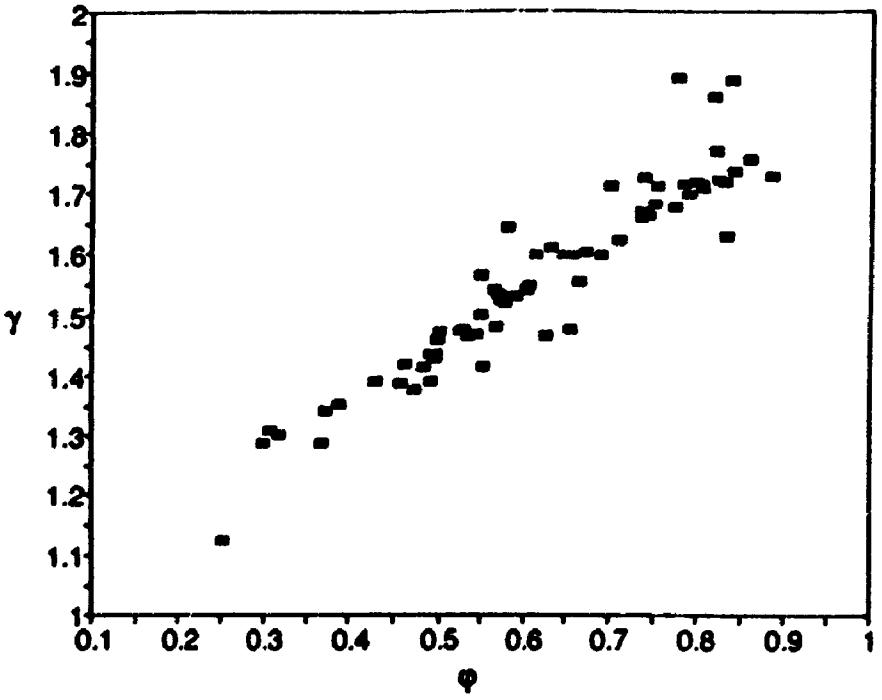


Figure 2.7: The exponent γ is plotted against the crossover exponent ϕ for triangular lattice (bond) with an impenetrable surface.

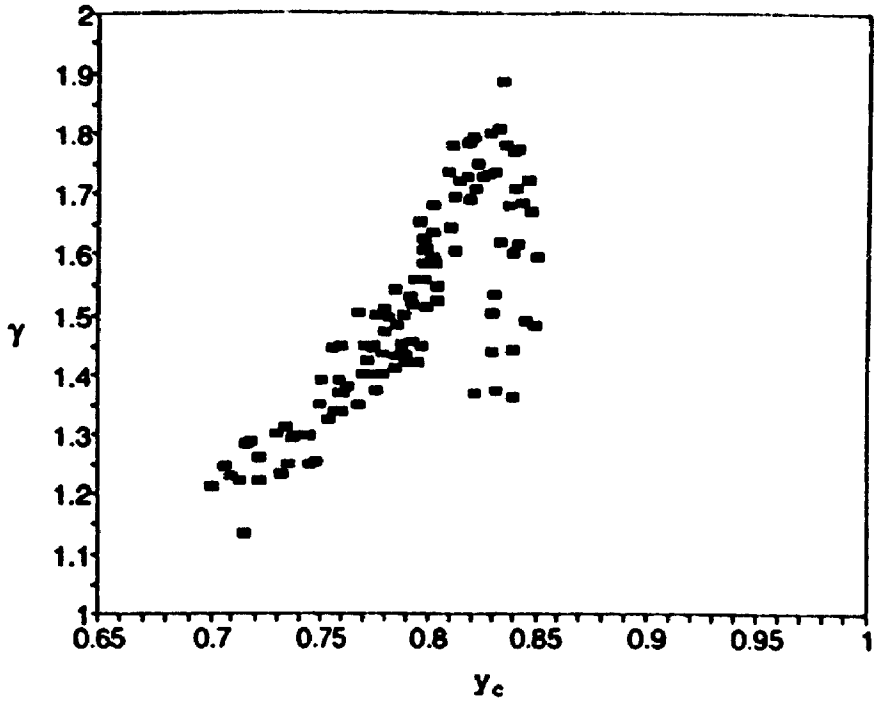


Figure 2.8: The exponent γ is plotted as a function of y_c for square lattice (bond) with an impenetrable surface.

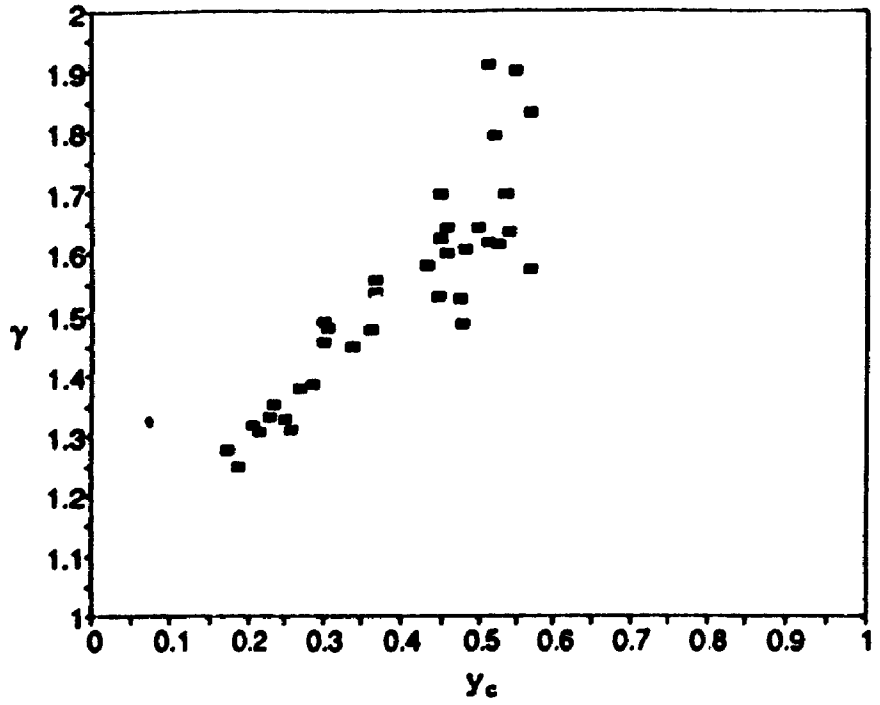


Figure 2.9: The exponent γ is plotted as a function of y_c for triangular lattice (bond) with a penetrable surface.

2.2.3 One-variable analysis for penetrable surfaces

The problem of estimating ϕ may be reduced to a one variable analysis if γ and the ratio y_c/x_c are known with sufficient accuracy, by differentiating the scaling function (2.55) with respect to y and setting the ratio y/x to its value at the critical point (Pfeuty *et al* [50]). The resulting function has a power law dependence on $(x_c - x)$ which may be analysed using standard one variable analysis techniques:

$$\frac{\partial f(x,y)}{\partial y}\Big|_{y/x=y_c/x_c} \sim (x_c - x)^{-(\gamma+\phi)} Z(0). \tag{2.73}$$

In the present case, we take the conjecture of Hammersley *et al* [32] that $\omega_c = 0$, i.e, $y_c = x_c$ for the penetrable surface problem and, consequently, γ has its bulk value which is known to a high accuracy. We have applied a number of standard one variable analysis techniques to the resulting series to this case. The results are summarized in columns (a) to (d) of Table 2.2. (We have included results for a number of lattices where the series are too short to allow a reasonable test of the PDA method or the PDA approximants are too scattered to give meaningful estimates). The data for these lattices are given in references [25], [38]. In the case of the impenetrable surface the ratio y_c/x_c is not known with sufficient accuracy to give us any confidence in this method).

The results for ϕ in columns (a) to (d) of Table 2.2 show reasonable consistency amongst themselves for a given lattice dimensionality but are too high to be consistent with the predictions $\phi(d = 2) = 0.25$ and $\phi(d = 3) = 0.408 \pm 0.002$ which result from the scaling relation $\phi = 1 - \nu$ where it is known that $\nu(d = 2) = 3/4$ and $\nu(d = 3) = 0.59$.

The only exception to this is the analysis of the square lattice site series by the Baker-Hunter method (Baker and Hunter [51]) which is consistent with the predicted value of $\phi = 1 - \nu$. Inspection of the approximants to the Baker-Hunter auxiliary function for the square lattice site series showed that a second pole on the real positive

axis is also resolved. This indicates that a confluent singularity is present and the position of this secondary pole provides an estimate of the exponent of this confluence (De'Bell *et al* [27], Baker and Hunter [51]). By plotting the position of the secondary pole against the position of the primary pole for the approximants considered and using the expected value of the leading exponent $\gamma + \phi = 51/32$, we estimate that the confluence has an exponent approximately equal to γ. The existence of a confluence with exponent γ is not surprising and will, in fact, always occur if the crossover function $Z(\Delta\tilde{y}/(\Delta\tilde{x})^{\phi})$ contains a multiplicative factor or additive term which is analytic in y.

To test the assumption that it is the influence of this confluence which results in the discrepancy with the expected value of ϕ, we have formed the series

$$f_1(x) = (x_c - x)^{\gamma} \frac{\partial f(x,y)}{\partial y} \tag{2.74}$$

with $y/x = 1$, which is expected to have the form

$$f_1(x) \sim (x_c - x)^{-\phi} + B(x), \tag{2.75}$$

where $B(x)$ is a (backgroud) term which is not singular at $x = x_c$. Estimates of ϕ obtained by a Baker-Hunter analysis of this series are shown in column (e) of Table 2.2. For both the two and three dimensional cases the results are in reasonable good agreement with the predicted value. That the central estimates in two dimensions are still a little high is perhaps not surprising since the singularity of the series analysed in this case is somewhat weak. The weak nature of the singularity also leads to difficulty in analysing the modified series by other methods. For example, if the Neville table method is used to analyse the square and simple cubic lattice series the columns of the table do not converge (for the number of terms presently available). This may be attributed to a singularity at $x = -x_c$ which, now is stronger than the singularity at $x = x_c$. Applying an Euler transform which moves the singularity on the negative axis to a position further from the origin results in reasonably converged Neville tables

with results consistent with those given in column (e) of Table 2.2.

The above one-variable analysis for the penetrable surfaces indicates that the presence of the confluent terms may be the source of the discrepancy in the results of Ishinabe [35].

Table 2.2: The estimates of ϕ for the body-centered-cubic (bcc), face-centered-cubic (fcc), simple cubic (sc), diamond (Di), triangular (T), and square (SQ) lattices from the one-variable analysis of the series $f'(x)$ described in section 2.2.3 by the method of (a) Neville tables, (b) $d\log$ Padé approximants (c) biased $d\log$ Padé approximants, (d) Baker-Hunter confluent singularity analysis. Estimates of ϕ contained applying the Baker-Hunter method to the modified series $(x_c - x)^{\gamma} f'(x)$ are reported in column (e).

Method / Lattice	a	b	c	d	e
			(a) Bond		
bcc	0.420 ± 0.020	0.450 ± 0.01	$0.450^{+0.010}_{-0.020}$	$0.480^{+0.030}_{-0.050}$	$0.380^{+0.030}_{-0.040}$
fcc	0.430 ± 0.008	0.463 ± 0.005	0.450 ± 0.020	0.480 ± 0.060	$0.386^{+0.007}_{-0.014}$
sc	$0.413^{+0.030}_{-0.015}$	0.444 ± 0.003	$0.440^{+0.020}_{-0.030}$	$0.510^{+0.050}_{-0.080}$	$0.350^{+0.060}_{-0.060}$
T	0.3062 ± 0.0035	0.3262 ± 0.003	$0.320^{0.002}_{-0.003}$	$0.323^{+0.002}_{-0.003}$	$0.270^{+0.003}_{-0.002}$
SQ	0.307 ± 0.004	0.317 ± 0.001	0.319 ± 0.001	$0.323^{+0.008}_{-0.009}$	0.290 ± 0.010
			(b) Site		
Di	0.473 ± 0.015	0.530 ± 0.010	$0.500^{+0.030}_{-0.010}$	0.510 ± 0.060	$0.420^{+0.020}_{-0.044}$
sc	0.470 ± 0.020	0.530 ± 0.010	0.480 ± 0.020	0.500 ± 0.080	0.400 ± 0.050
SQ	0.356 ± 0.005	0.370 ± 0.010	0.375 ± 0.010	0.263 ± 0.013	0.270 ± 0.040

Chapter 3

Polymer networks with specified topologies

3.1 Introduction

In this chapter, we consider polymer networks whose topology is specified in terms of c cycles, b_3 vertices of degree 3, ..., b_{2d} vertices of degree $2d$. These vertices are also referred to as branch points. These quantities are simply related together by Euler's formula:

$$2c = 2 - b_1 + \sum_{i=3}^{2d}(i-2)b_i, \tag{3.1}$$

$$2K = b_1 + \sum_{i=3}^{2d} i b_i, \tag{3.2}$$

where b_1 is the number of vertices of degree 1 and K is the number of chains connecting the branch points and the vertices of degree 1. The values do not specify a unique topology since they do not uniquely determine the connectivity. More than one topology may have the same set of values (see Figure 1.1 (c), (d)).

Such a network with each chain of uniform length has been studied by Duplantier [11] and Duplantier and Saleur [12]. They have conjectured the dependence of the critical exponent γ_g on the values $\{c, b_3, \ldots, b_{2d}\}$ and obtained exact results in two dimensional geometry by invoking conformal invariance. Ohno and Binder [28] have rederived the same scaling form for such a polymer network by using the equivalence

between the generating function for the number of configurations and the correlation function for the classical N-component model in the limit $N \to 0$.

The corresponding nonuniform polymer network with total length n has been studied by Gaunt *et al* [13] and Lipson and Whittington [14]. From their exact enumeration analysis and some heuristic arguments, Gaunt *et al* [13] have conjectured that for a network with a number of cut-edges, its critical exponent is given by

$$\gamma_g = \gamma + b - 1, \tag{3.3}$$

where γ is the exponent for SAW and b is the number of cut edges in a network G (a cut edge, if removed, disconnects G). In section 3.2 of this chapter, we consider a polymer network called a twin-tailed tadpole and show rigorously that its critical exponent satisfies (3.3).

In the remainder of the chapter, we study the effects of the topology on the reduced free energy of polymer networks interacting with a surface. We will show that for $d \geq 3$, such polymer networks have the same reduced free energy as self-avoiding walks. For $d = 2$, the reduced free energy can be different from that for SAWs. However, we will take 3-stars and H-combs (see Figure (a), (b)) as examples to show that provided their reduced free energies exist, they will have the same transition point and crossover exponent as that for walks. Parts of the work included in this chapter have previously appeared in Zhao and Lookman [52], [53].

3.2 The critical exponent for twin-tailed tadpoles

An n-step twin-tailed tadpole is the network with the topology $c = 1$ and $b_4 = 1$ (Figure 3.1).

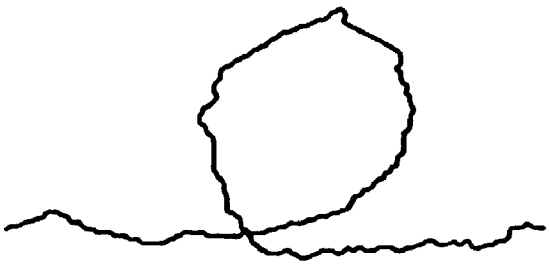


Figure 3.1: Example of a twin-tailed tadpole

It has two cut-edges, i.e. $b = 2$. By denoting by t_n the number of n-step twin-tailed tadpoles, Gaunt *et al* [13] have shown that

$$\lim_{n\to\infty} \frac{1}{n} \ln t_n = \lim_{n\to\infty} \frac{1}{n} \ln c_n = \kappa, \tag{3.4}$$

and

$$\gamma_t \leq \gamma + 1, \tag{3.5}$$

where γ_t is the exponent for twin-tailed tadpoles. From their conjecture (3.3), one would expect that

$$\gamma_t = \gamma + 1. \tag{3.6}$$

In the following, by using a corollary from Kesten's pattern theorem [54], we will show that

$$\gamma_t \geq \gamma + 1. \tag{3.7}$$

Combining it with (3.5) yields (3.6).

3.2.1 Pattern theorem

A *pattern* **P** is a prescribed finite step walk and is said to *occur* in a self-avoiding walk **W** if it is sub-SAW of **W**. It is said that **P** *occurs r times* in **W** if **P** appears at r distinct steps, and the vertices of any two copies of **P** are disjoint or the terminal vertex of one is the initial vertex of another. **P** is called a *Kesten pattern* if there exists an n-step walk **W** where **P** appears more than twice in **W**.

Theorem 3.1 (Kesten [54]) *If* **P** *is any (finite) pattern and* $c_n(\varepsilon, \mathbf{P}, \leq)$ *is the number of* n*-step self-avoiding walks in which the pattern* **P** *occurs at most* εn *times, then there exists a value of* $\varepsilon_0 > 0$ *such that*

$$\lim_{n\to\infty} \sup \frac{1}{n} \ln c_n(\varepsilon_0, \mathbf{P}, \leq) < \kappa \tag{3.8}$$

provided that there exists a self-avoiding walk in which **P** *occurs more than twice.*

The theorem has proved useful in lattice statistics, for example, in the study of walks confined to a subset of a lattice (Hammersley and Whittington [55]). The corollary of Kesten's theorem we require is as follows:

Corollary 3.1 *For the same value of* ε_0*, let* $c_n(\varepsilon_0, \mathbf{P}, >)$ *be the number of* n*-step self-avoiding walks in which the same pattern* **P** *appears more than* $\varepsilon_0 n$ *times, then*

$$\lim_{n\to\infty} \frac{c_n(\varepsilon_0, \mathbf{P}, >)}{c_n} = 1. \tag{3.9}$$

Proof: From theorem 3.1, there exists a value of $\delta > 0$ and an integer of N such that for any $n > N$, we have

$$0 < c_n(\varepsilon_0, \mathbf{P}, \leq) \leq e^{n(\kappa-\delta)}. \tag{3.10}$$

Since

$$\frac{c_n(\varepsilon_0, \mathbf{P}, >)}{c_n} = 1 - \frac{c_n(\varepsilon_0, \mathbf{P}, \leq)}{c_n}, \tag{3.11}$$

by using (3.10), we obtain that

$$1 - \frac{e^{n(\kappa-\delta)}}{c_n} \leq \frac{c_n(\varepsilon_0, \mathbf{P}, >)}{c_n} < 1. \tag{3.12}$$

Taking limits yields, from (3.4),

$$1 \leq \liminf_{n\to\infty} \frac{c_n(\varepsilon_0, \mathbf{P}, >)}{c_n} \leq \limsup_{n\to\infty} \frac{c_n(\varepsilon_0, \mathbf{P}, >)}{c_n} \leq 1, \tag{3.13}$$

which gives (3.9).

3.2.2 The critical exponent for twin-tailed tadpoles

Now we are ready to prove (3.7) by using the above theorem and corollary with the assumption that γ exists.

We define a pattern $\mathbf{P}$ by

$$\begin{aligned} \mathbf{P} \;=\; & \{\mathbf{x}+\mathbf{e}_d,\ \mathbf{x}+2\mathbf{e}_d,\ \mathbf{x}+2\mathbf{e}_d+\mathbf{e}_{d-1},\ \mathbf{x}+2\mathbf{e}_d+2\mathbf{e}_{d-1},\\ & \mathbf{x}+\mathbf{e}_d+2\mathbf{e}_{d-1},\ \mathbf{x}+\mathbf{e}_d+\mathbf{e}_{d-1},\ \mathbf{x}+\mathbf{e}_{d-1}\mathbf{x}+2\mathbf{e}_{d-1},\\ & \mathbf{x}+3\mathbf{e}_{d-1}\} \end{aligned} \tag{3.14}$$

(Figure 3.2(a)). It is self-avoiding walk and can occur more than twice in a SAW, for instance, it occurs three times in the SAW $\mathbf{W} = \mathbf{PPP}$ (Figure 3.2(b)). Therefore, from the theorem, it can occur infinitely often in an infinite SAW. If we denote by $c_n(\varepsilon, \mathbf{P}, >)$ the number of SAWs in which $\mathbf{P}$ occurs more than εn times, from the corollary, there exists $\varepsilon_0 > 0$ such that for sufficiently large n,

$$c_n = c_n(\varepsilon_0, \mathbf{P}, >)(1 + o(1)). \tag{3.15}$$

Consider an n-step self-avoiding walk $\mathbf{W}$ on which $\mathbf{P}$ occurs more than εn times. We choose one of them. By deleting the edges $[\mathbf{x}+\mathbf{e}_d,\ \mathbf{x}+2\mathbf{e}_d]$ and $[\mathbf{x}+2\mathbf{e}_d,\ \mathbf{x}+2\mathbf{e}_2+\mathbf{e}_{d-1}]$ and adding the edges $[\mathbf{x}+\mathbf{e}_d,\ \mathbf{e}_d+\mathbf{e}_{d-1}]$ and $[\mathbf{x}+\mathbf{e}_d+\mathbf{e}_{d-1},\ \mathbf{x}+\mathbf{e}_d+2\mathbf{e}_{d-1}]$, we convert $\mathbf{W}$ into a distinct n-step twin-tailed tadpole (Figure 3.2(c)). Therefore, we obtain

$$t_n \geq (\varepsilon n) c_n(\varepsilon, \mathbf{P}, >). \tag{3.16}$$

Then, from (3.15), we have

$$t_n \geq (\varepsilon_0 n) c_n. \tag{3.17}$$

Combining it with (3.4) yields

$$\gamma_t \geq \gamma + 1. \tag{3.18}$$

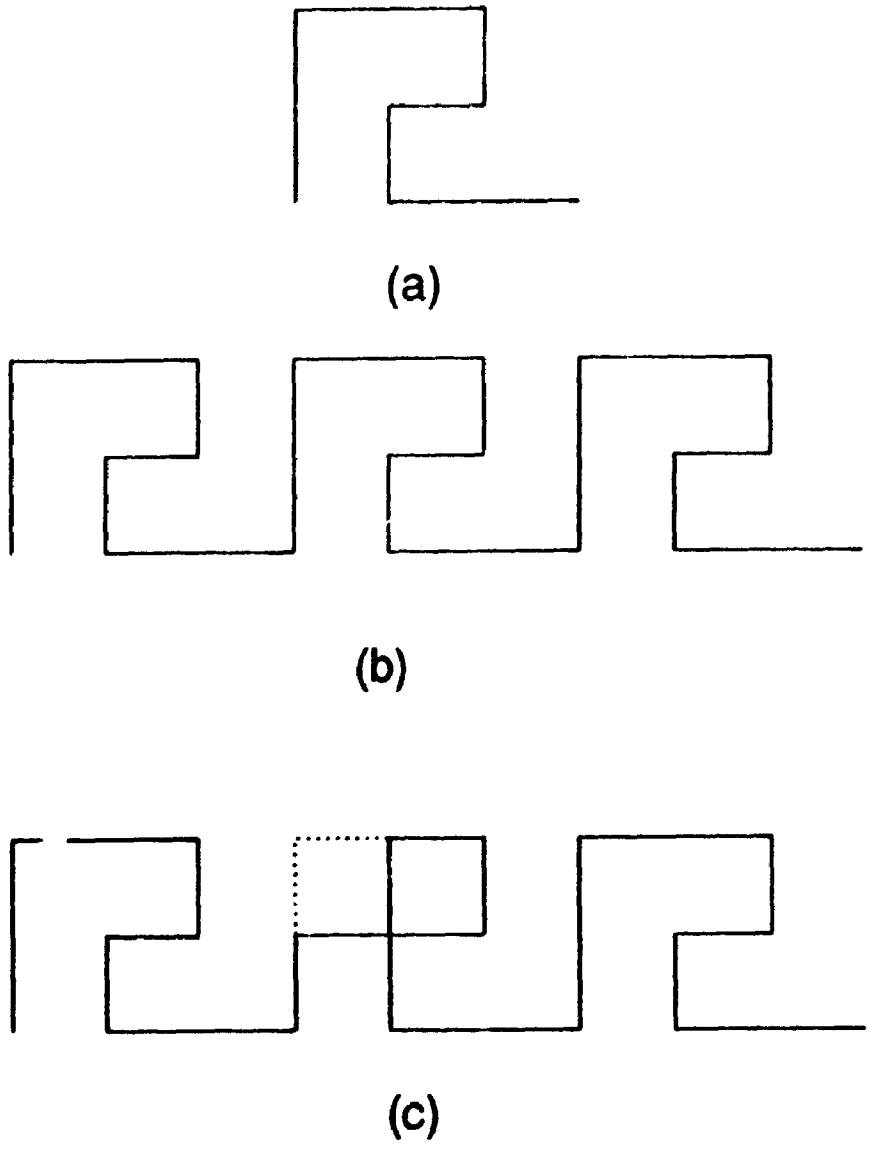


Figure 3.2: (a) the pattern **P**; (b) a walk having the pattern **P** occurring three times; (c) conversion of the walk in (b) into a twin-tailed tadpole at one pattern.

The proof of (3.6) for twin-tailed tadpoles gives a nontrivial analytic example to the conjecture (3.3) which still remains a conjecture.

3.3 The interaction of uniform polymer topologies with a surface: $d \geq 3$

We consider a uniform polymer network $\mathbf{G}_n(c, b_3, \ldots, n_{2d})$ interacting with a penetrable surface. In this case, each chain in the network G is an n-step self-avoiding walk. For $c = 0$, each chain in such a network has a different initial and terminal vertex and therefore, each chain can have either even or odd number of vertices. The case $c \neq 0$ includes those with loops in which the initial and terminal vertices of a chain are the same. Chains forming loops or polygons must have an even number of vertices for non-zero embeddings in a hypercubic lattice. Hence, for a uniform topology with $c \neq 0$, we restrict all chains to have an even number of vertices.

Let $g_{n,m}$ be the number of such networks with n edges in each chain and a total $m + 1$ vertices in the surface. We define

$$G_N(c, b_3, \ldots, b_{2d}, \omega) = \sum_{m=0}^{N} g_{n,m} e^{m\omega}, \tag{3.19}$$

where $N = nK - c + 1$ is the total number of vertices in a uniform network.

We show that

$$\lim_{n\to\infty} \frac{1}{n} \ln G_N(c, b_3, \ldots, b_{2d}, \omega) = A(\omega), \tag{3.20}$$

where $A(\omega)$ is given in (2.3) and for $c \neq 0$, the limit is taken through even value of n only.

First, we derive a **lower bound** for the partition function $G_N(c, b_3, \ldots, b_{2d}, \omega)$, which is obtained as follows. We consider some special walks with certain constraints and show that such walks have the same reduced free energy $A(\omega)$. Then, we construct some simple polymer topologies which we call *components* from the special walks. Finally, using these components and following a procedure analogous to that of Gaunt *et al* [13], we construct a polymer network with the set $\{c, b_3, \ldots, b_{2d}\}$ which yields a lower bound for $G_N(c, b_3, \ldots, b_{2d}, \omega)$. In the following, we consider the case $c \neq 0$.

3.3.1 Self-avoiding walks confined in a wedge

We define a wedge by

$$\mathcal{W}: \quad 1 \leq x_2, \ \ldots, \ 1 \leq x_{d-1} \leq x_d, \tag{3.21}$$

and consider a self-avoiding walk $\mathbf{W}$ which is confined in $\mathcal{W}$ and satisfies,

(a) $\mathbf{x}(0) = \mathbf{e}_2 + \mathbf{e}_3 + \cdots + \mathbf{e}_{d-1} + 4\mathbf{e}_d$;

(b) for $\mathbf{x}(i)$, $1 \leq i \leq n-1$,

$$x_d(0) < x_d(i) \leq x_d(n), \tag{3.22}$$

and

$$x_{d-1}(i) < x_d(i); \tag{3.23}$$

(c) for $\mathbf{x}(n)$,

$$x_d(n) = x_{d-1}(n). \tag{3.24}$$

An example of such a walk is given in Figure 3.3.

Lemma 3.1 *Let $\mathcal{B}_n$ be the set of all such n-step walks and $\mathcal{B}_{n,m}$ the subset of $\mathcal{B}_n$ where a member of it has $m+1$ vertices in the surface. We denote by $b_{n,m}$ the number of walks in $\mathcal{B}_{n,m}$ and define*

$$B_n(\omega) = \sum_{m=0}^{n} b_{n,m} e^{m\omega}, \tag{3.25}$$

then

$$\lim_{n\to\infty} \frac{1}{n} \ln B_n(\omega) = A(\omega). \tag{3.26}$$

Proof: Let $\mathcal{D}^{(1)}_{n,m}$ be the set of all n-step walks confined in $\mathcal{W}$ with $\mathbf{x}(0) = \mathbf{e}_2 + \cdots + \mathbf{e}_d$ and with $m+1$ vertices in the surface. We denote by $d^{(1)}_{n,m}$ the number of walks in $\mathcal{D}^{(1)}_{n,m}$. It has been shown (Whittington and Soteros [56]) that

$$\lim_{n\to\infty} \frac{1}{n} \ln D^{(1)}_n(\omega) = \lim_{n\to\infty} \frac{1}{n} \ln \sum_{m=0}^{n} d^{(1)}_{d,m} e^{m\omega} = A(\omega). \tag{3.27}$$

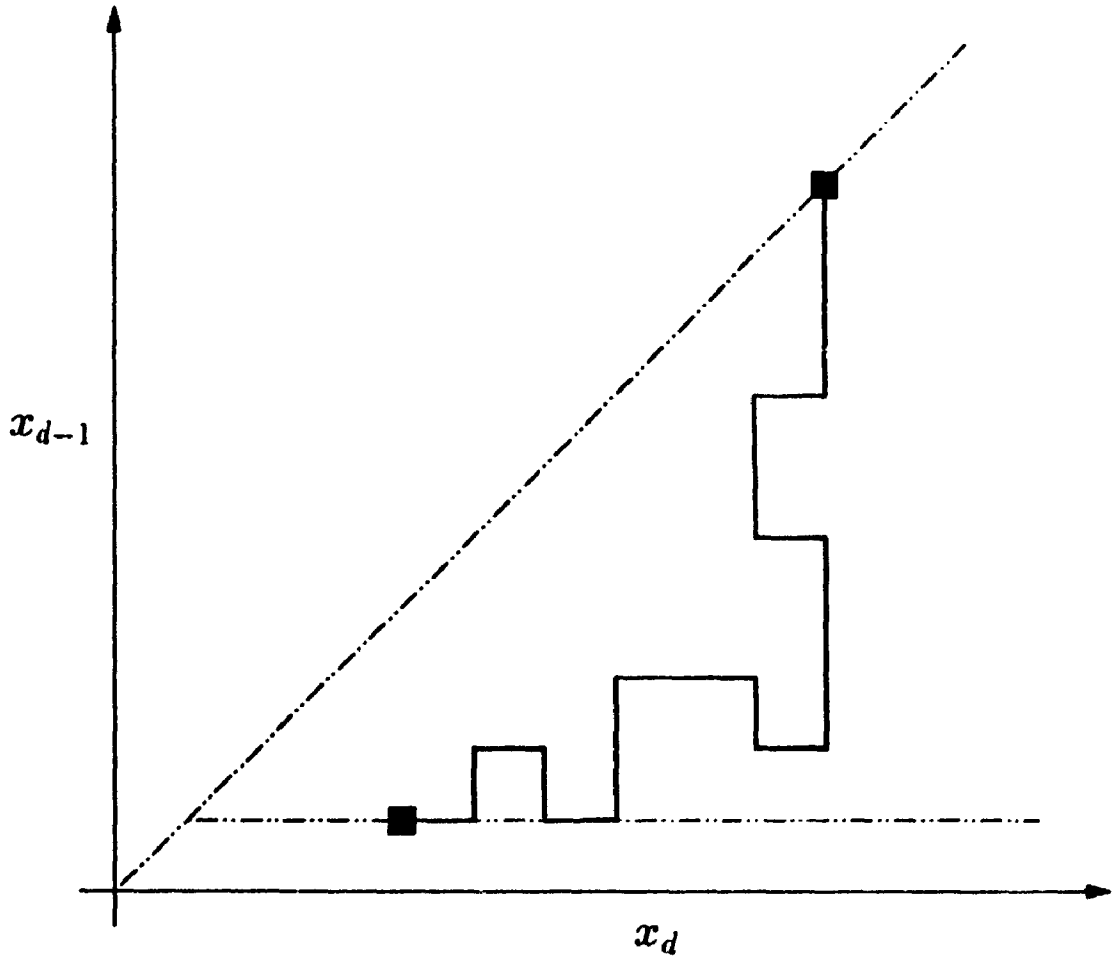


Figure 3.3: Example of a self-avoiding walk (full line) defined by (a)-(b) confined in the wedge defined in (3.21). The dashed lines represent the hyperplane $x_{d-1} = x_d$ and $x_{d-1} = 1$.

Consider a walk $\mathbf{W} = \{\mathbf{x}(0), \mathbf{x}(1), \ldots, \mathbf{x}(n)\}$ in $\mathcal{D}^{(1)}_{n,m}$. Since it is confined in the wedge defined in (3.21), it satisfies,

$$\begin{aligned} & x_{d-}(0) = x_d(0) \\ & x_{d-1}(0) \le x_{d-1}(i), \quad x_{d-1}(i) \le x_d(i), \quad i = 1, \ldots, n. \end{aligned} \tag{3.28}$$

Let j be the largest integer such that $x_{d-1}(j) + x_d(j) = \max_i\{x_{d-1}(i) + x_d(i)\}$. By reflecting the segment $\{\mathbf{x}(j), \ldots, \mathbf{x}(n)\}$ in the hyperplane $x_d + x_{d-1} = x_d(j) + x_{d-1}(j)$, we obtain a new walk $\mathbf{W}'$ such that for $i \ge j$

$$\mathbf{x}'(i) = \mathbf{x}(j) + [x_d(j) - x_d(i)]\mathbf{e}_{d-1} + [x_{d-1}(j) - x_{d-1}(i)]\mathbf{e}_d. \tag{3.29}$$

Therefore,

$$\begin{aligned} x'_d(i) - x'_{d-1}(i) &= x_d(j) + x_{d-1}(j) - x_{d-1}(i) \\ &\quad -[x_{d-1}(j) + x_d(j) - x_d(i)] \\ &= x_d(i) - x_{d-1}(i) \\ &\ge 0. \end{aligned} \tag{3.30}$$

Also, it can be shown that $\mathbf{W}'$ has the same number of vertices in the surface as $\mathbf{W}$ (because a reflection does not change any x_1 coordinate). Hence, $\mathbf{W}'$ is confined in the wedge $\mathcal{W}$ and is a member of $\mathcal{D}^{(1)}_{n,m}$. We continue in this fashion until eventually, we obtain a new walk $\mathbf{W}''$ such that $x''_{d-1}(n) + x''_d(n) = \max_i\{x''_{d-1}(i) + x''_d(i)\}$. We add one extra step in the $\mathbf{e}_d$ direction to the end of $\mathbf{W}''$. The resulting walk has either $m+1$ or $m+2$ vertices in the surface and satisfies, for any $i < n+1$,

$$x_{d-1}(n+1) + x_d(n+1) > x_{d-1}(i) + x_d(i). \tag{3.31}$$

We denote by $\mathcal{D}^{(2)}_n$ the set of all such n-step walks and by $b^{(2)}_{n,m}$ the number of walks in $\mathcal{D}^{(2)}_n$ with $m+1$ vertices in the surface. From Hammersley and Welsh [57], there exists a constant $c > 0$ such that

$$d^{(1)}_{n,m} \le e^{c\sqrt{n}}[d^{(2)}_{n+1,m} + d^{(2)}_{n+1,m+1}]. \tag{3.32}$$

Hence,

$$D_n^{(1)}(\omega) \le e^{c\sqrt{n}}(1+e^{-\omega})D_{n+1}^{(2)}(\omega). \tag{3.33}$$

The next step is to partition $\mathcal{D}_n^{(2)}$ into subclasses by placing two walks in the same subclass if they have the same final point. Such an n-step walk starting from $\mathbf{e}_2+\cdots+\mathbf{e}_d$, must be totally confined in a hyper-prism given by:

$$-n \le x_1 \le n,\ 1 \le x_2 \le n+1,\ \ldots,\ 1 \le x_{d-2} \le n+1,\ 1 \le x_{d-1} \le x_d \le n+1. \tag{3.34}$$

There are at most $I = (2n+1)(n+1)^{d-1}/4$ subclasses. For given i, consider two walks $\mathbf{W}_1$ and $\mathbf{W}_2$ both belonging to the ith subclass of $\mathcal{D}_n^{(2)}$ and having m_1+1 and m_2+1 vertices in the surface respectively. Let $\mathbf{x}(n) = (x_1, \ldots, x_d)$ be their end point. We reflect $\mathbf{W}_2$ in the hyperplane $x_{d-1}+x_d = x_{d-1}(n)+x_d(n)$. From (3.28)–(3.31), one can show that it yields a $2n$-step walk $\mathbf{W}'$ such that its first and last points are on the hyperplane $x_{d-1} = x_d$, and for $1 \le j \le n-1$, $x'_{d-1}(j) \le x'_d(j)$, $x'_d(j) \le x'_d(2n)$. $\mathbf{W}'$ can have either m_1+m_2+1 or m_1+m_2+2 vertices in the surface depending on the position of $\mathbf{x}(n)$. We body shift $\mathbf{W}'$ to let $\mathbf{x}'(0)$ be at the vertex $\mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+5\mathbf{e}_d$. By adding an extra step to connect $\mathbf{x}'(0)$ with the vertex $\mathbf{x}'(0)-\mathbf{e}_d$ and three steps to connect $\mathbf{x}'(2n)$ with the vertex $\mathbf{x}'(2n)+3\mathbf{e}_{d-1}$, we obtain a member of $\mathcal{B}_{2n+4}$, which has either m_1+m_2+5 or m_1+m_2+6 vertices in the surface. Each distinct pair of walks $\mathbf{W}_1$ and $\mathbf{W}_2$ will yield a distinct member of $\mathcal{B}_{2n+4}$ in this way. We denote by $d_{n,m}^{(2)}(i)$ the number walks in the ith subclass with $m+1$ vertices in the surface. We obtain

$$d_{n,m_1}^{(2)}(i)d_{n,m_2}^{(2)}(i) \le b_{2n+4,m_1+m_2+4} + b_{2n+4,m_1+m_2+5}. \tag{3.35}$$

Write

$$D_n^{(2)}(\omega,i) = \sum_{m=0}^{n} d_{n,m}^{(2)}(i)e^{m\omega}. \tag{3.36}$$

From (3.35), we obtain

$$[D_n^{(2)}(\omega,i)]^2 = \sum_{m_1=0}^{n}\sum_{m_2=0}^{n} d_{n,m_1}^{(2)}(i)d_{n,m_2}^{(2)}(i)e^{(m_1+m_2)\omega}$$

$$\leq \sum_{m_1=0}^{n}\sum_{m_2=0}^{n}(b_{2n+4,m_1+m_2+4}+b_{2n+4,m_1+m_2+5})e^{(m_1+m_2)\omega}$$
$$\leq e^{4|\omega|}(1+e^{|\omega|})\sum_{m=0}^{2n+4}(m+1)b_{2n+4,m}e^{m\omega}$$
$$\leq (2n+4)e^{4|\omega|}(1+e^{|\omega|})B_{2n+4}(\omega), \tag{3.37}$$

and hence, by Cauchy's inequality

$$[D_n^{(2)}(\omega)]^2 = \left(\sum_{i=1}^{I} D_n^{(2)}(\omega,i)\right)^2 \leq \sum_{i=1}^{I}1^2\sum_{i=1}^{I}[D_n^{(2)}(\omega,i)]^2$$
$$\leq I^2(2n+4)e^{4|\omega|}(1+e^{|\omega|})B_{2n+4}(\omega)$$
$$\leq (2n+4)^d e^{4|\omega|}(1+e^{|\omega|})B_{2n+4}(\omega), \tag{3.38}$$

or

$$D_n^{(2)}(\omega) \leq (2n+4)^{d/2}e^{2|\omega|}(1+e^{|\omega|})^{1/2}B_{2n+4}(\omega)^{1/2}. \tag{3.39}$$

From (3.33), we obtain

$$D_n^{(1)}(\omega) \leq [2(n+1)+4]^{d/2}e^{(2|\omega|+c\sqrt{n})}(1+e^{|\omega|})^{3/2}B_{2(n+1)+4}(\omega)^{1/2}. \tag{3.40}$$

On the other hand, by adding a 3-step walk: $\{\mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+\mathbf{e}_d,\ \mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+2\mathbf{e}_d,\ \ldots,\ \mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+4\mathbf{e}_d\}$ to a member of $\mathcal{B}_{n,m}$, we obatain a distinct member of $\mathcal{D}_{n+3,m+3}$. Hence, we have

$$b_{n,m} \leq d^{(1)}_{n+3,m+3}, \tag{3.41}$$

and therefore,

$$B_n(\omega) \leq e^{-3\omega}D^{(1)}_{n+3}(\omega). \tag{3.42}$$

Combining it with (3.27) and (3.40), we establish (3.26).

3.3.2 Construction of components

Definition 3.1 *1) f_{ij} and g_i are maps such that, for* $\mathbf{x} = (x_1, \ldots, x_i, \ldots, x_j, \ldots, x_d)$,

$$f_{ij}(\mathbf{x}) = (x_1, \ldots, x_j, \ldots, x_i, \ldots, x_d), \qquad i,\ j \geq 2 \tag{3.43}$$

and

$$g_i(\mathbf{x}) = (x_1, \ldots, -x_i, \ldots, x_j, \ldots, x_d), \qquad i \geq 1. \tag{3.44}$$

2) For any sequence of vertices $\mathbf{W} = \{\mathbf{x}(0), \ldots, \mathbf{x}(n)\}$,

$$f_{ij}(\mathbf{W}) = \{f_{ij}(\mathbf{x}(0)), \ldots, f_{ij}(\mathbf{x}(n))\}' \tag{3.45}$$

$$g_i(\mathbf{W}) = \{g_i(\mathbf{x}(0)), \ldots, g_i(\mathbf{x}(n))\}. \tag{3.46}$$

By this definition, the map f_{ij} interchanges the coordinates x_i, x_j and g_i replaces the coordinate x_i by $-x_i$. These lead to the following lemma in a straightforward manner.

Lemma 3.2 *(a) The maps f_{ij} and g_i are injective. (b) If* $\mathbf{W}$ *is a given self-avoiding walk, the image* $\mathbf{W}'$ *of* $\mathbf{W}$ *under these mappings is still a self-avoiding walk, and* $\mathbf{W}'$ *and* $\mathbf{W}$ *have the same number of vertices (or edges) in the surface $x_1 = 0$.*

We also define two links L_1 and L_2 which are two fixed $(d+4)$-step self-avoiding walks given by

$$\begin{aligned} L_1 \;=\; \{&\mathbf{0},\ \mathbf{e}_1,\ \mathbf{e}_1 + \mathbf{e}_d,\ \mathbf{e}_1 + 2\mathbf{e}_d,\ \mathbf{e}_1 + 3\mathbf{e}_d,\ \mathbf{e}_1 + 4\mathbf{e}_d, \\ &\mathbf{e}_1 + \mathbf{e}_{d-1} + 4\mathbf{e}_d,\ \ldots,\ \mathbf{e}_1 + \mathbf{e}_2 + \cdots + \mathbf{e}_{d-1} + 4\mathbf{e}_d, \\ &\mathbf{e}_2 + \cdots + \mathbf{e}_{d-1} + 4\mathbf{e}_d\}; \end{aligned} \tag{3.47}$$

$$\begin{aligned} L_2 \;=\; \{&\mathbf{0},\ \mathbf{e}_d,\ 2\mathbf{e}_d,\ \mathbf{e}_{d-1} + 2\mathbf{e}_d,\ \mathbf{e}_{d-1} + 3\mathbf{e}_d,\ 3\mathbf{e}_d,\ 4\mathbf{e}_d, \\ &\mathbf{e}_{d-1} + 4\mathbf{e}_d,\ \ldots,\ \mathbf{e}_2 + \cdots + \mathbf{e}_{d-2} + \mathbf{e}_{d-1} + 4\mathbf{e}_d\}. \end{aligned} \tag{3.48}$$

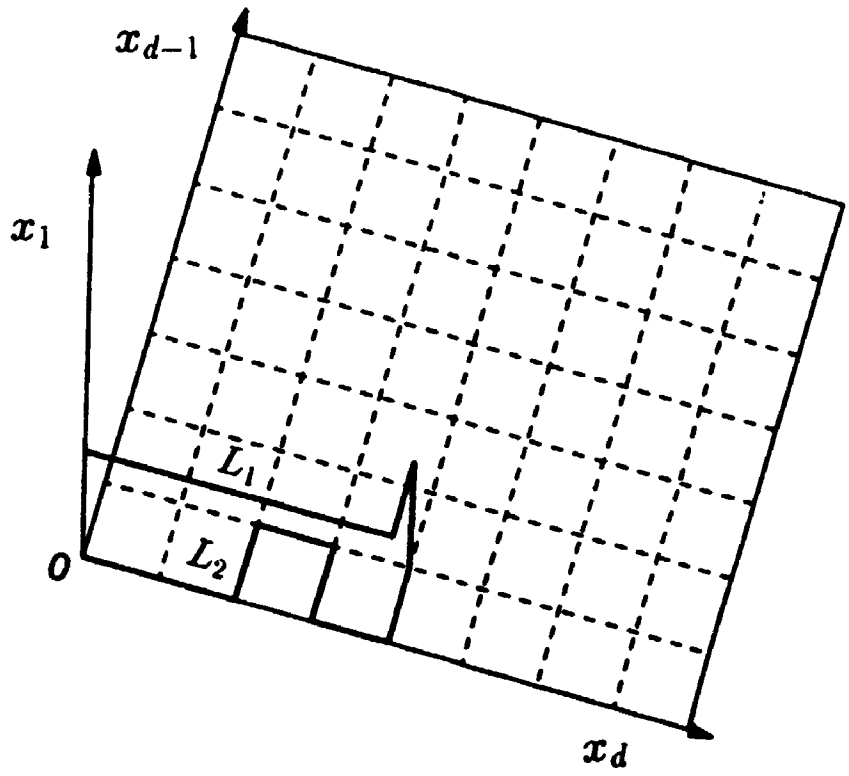


Figure 3.4: Full lines represents the finite walks L_1 and L_2 defined in (3.47) and (3.48).

L_1 has two vertices in the surface $x_1 = 0$, while L_2 is totally embedded in the surface. The two walks intersect only at the points $\mathbf{0}$ and $\mathbf{x}(0) = \mathbf{e}_2 + \cdots + \mathbf{e}_{d-1} + 4\mathbf{e}_d$. Concatenating L_1 (or L_2) with one walk in $\mathcal{B}_{n,m}$ results in an $(n + d + 4)$-step walk with $m+1$ (or $m+d+4$) vertices in the surface and with the edge $[\mathbf{0}, \mathbf{e}_1]$ (or $[\mathbf{0}, \mathbf{e}_d]$) as its first step (Figure 3.4).

We partition $\mathcal{B}_n$ into subclasses by placing two walks in the same subclass, if they have the same final point. By the definition of $\mathcal{B}_n$, there are at most K =

the end vertex of all the walks. By using walks from the same $\mathcal{B}_n^i$, we construct three different types of components.

The first type component

The first type component that we need is a $2(n+d+6)$-step polygon p, which is obtained as follows. We take two walks $\mathbf{W}_1$ and $\mathbf{W}_2$ from $\mathcal{B}_n^i$ and concatenate either both of them with L_1 or $\mathbf{W}_1$ with L_1 and $\mathbf{W}_2$ with L_2, which gives two $(n+d+4)$-step walks $\mathbf{W}_1'$, $\mathbf{W}_2'$. We define

$$\begin{aligned} \mathbf{W}_1'' &= g_{i_1} \cdots g_{i_k} f_{i,d-1} f_{j,d}(\mathbf{W}_1'), \\ \mathbf{W}_2'' &= g_{i_1} \cdots g_{i_k} f_{d-1,d} f_{j,d-1} f_{i,d}(\mathbf{W}_2'). \end{aligned} \tag{3.50}$$

The two new walks $\mathbf{W}_1''$ and $\mathbf{W}_2''$ intersect only at the origin $\mathbf{0}$ and the vertex $(x_1^*, \ldots, -x_{i_1}^*, \ldots, -x_{i_k}^*, \ldots, x_i^*, x_j^*)$ and form a $2(n+d+4)$-step polygon, which is totally confined in the octant given by

$$x_2 \geq 0, \ \ldots, \ x_{i_1} \leq 0, \ \ldots, \ x_{i_k} \leq 0, \ldots, \ x_d \geq 0. \tag{3.51}$$

Then we delete the last edge from $\mathbf{W}_2''$ and join the vertices $\mathbf{x}_2''(n-1)$ and $\mathbf{x}_1''(n)$ by a 5-step walk: $\{\mathbf{x}_2''(n-1), \ \mathbf{x}_2''(n-1)+\mathbf{e}_{d-1}, \ \mathbf{x}_2''(n-1)+\mathbf{e}_{d-1}+\mathbf{e}_d, \ \mathbf{x}_2''(n-1)+ +\mathbf{e}_{d-1}+2\mathbf{e}_d, \ \mathbf{x}_1''(n)\}$. This yields a $2(n+d+6)$-step polygon. Its incident edges at $\mathbf{0}$ are the edges $[\mathbf{0}, \ \mathbf{e}_i]$ (or $[\mathbf{0}, \ -\mathbf{e}_i]$) and $[\mathbf{0}, \ \mathbf{e}_j]$ (or $[\mathbf{0}, \ -\mathbf{e}_j]$) with $\mathbf{e}_i \cdot \mathbf{e}_j = 0$. We denote it by $\mathbf{P}(\pm\mathbf{e}_i, \pm\mathbf{e}_j)$. The signs indicate the corresponding incident edges at $\mathbf{0}$ (Figure 3.5). From the definition for walks in $\mathcal{B}_n^i$, one can verify that for any two vertices $\mathbf{x}(k_1)$, $\mathbf{x}(k_2)$ of $\mathbf{P}$,

$$| \, x_i(k_1) - x_i(k_2) \, | \leq x_d^*(n) + 1, \quad i = 1, \ \ldots, \ d. \tag{3.52}$$

We denote by $\mathcal{P}^1$ the set of all polygons obtained in this way.

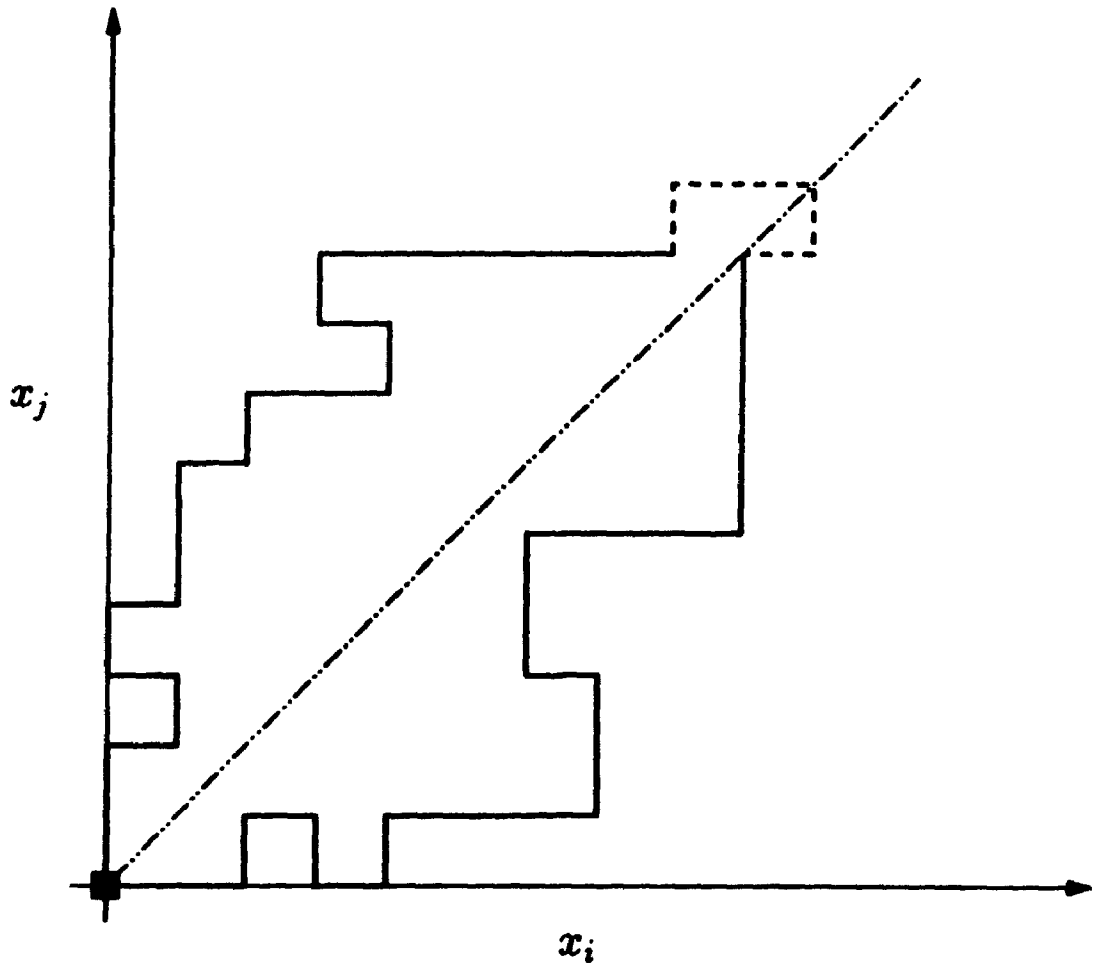


Figure 3.5: Example of a polygon $\mathbf{P}(\mathbf{e}_i, \mathbf{e}_j)$ obtained from two walks of $\mathcal{B}_n^t$.

The second type component

The second type component consists of two kinds of $2(n+d+6)$-step self-avoiding walks $\mathbf{W}^1$ and $\mathbf{W}^2$.

Construction of $\mathbf{W}^1$. We take two walks $\mathbf{W}_1$ and $\mathbf{W}_2$ from $\mathcal{B}_n^1$. We concatenate both of them by the same L_i $(i = 1, 2)$ and denote them by $\mathbf{W}_1'$ and $\mathbf{W}_2'$. We reflect $\mathbf{W}_2'$ in the hyperplane $x_d = x_d^*(n)$ to get a new walk $\mathbf{W}_2''$ such that its first (last) vertex is the reflection of the last (first) vertex of $\mathbf{W}_2''$. We delete the last edge from $\mathbf{W}_1'$ and the first edge from $\mathbf{W}_2''$ and body shift $\mathbf{W}_2''$ in the $\mathbf{e}_d$ direction by 4 steps. We join the two walks $\mathbf{W}_1'$ and $\mathbf{W}_2''$ with a 6-step walk: $\{\mathbf{x}_1''(n-1),\ \mathbf{x}_1''(n-1)+\mathbf{e}_d,\ \mathbf{x}_1''(n-1)+\mathbf{e}_d+\mathbf{e}_{d-1},\ \mathbf{x}_1''(n-1)+2\mathbf{e}_d+\mathbf{e}_{d-1},\ \ldots,\ \mathbf{x}_1''(n-1)+5\mathbf{e}_d-\mathbf{e}_{d-1},\ \mathbf{x}_1''(n-1)+5\mathbf{e}_d,\ \mathbf{x}_2''(2)\}$, which yields a $2(n+d+6)$-step walk. The new walk has its start vertex at $\mathbf{x}(s) = \mathbf{0}$ and its end vertex at $\mathbf{x}(e) = (0, 0, \ldots, 2x_d^*(n)+4)$. The incident edges at these two vertices are $[\mathbf{x}(s),\ \mathbf{x}(s)+\mathbf{e}_1]$ or $[\mathbf{x}(s),\ \mathbf{x}(s)+\mathbf{e}_d]$ and $[\mathbf{x}(e),\ \mathbf{x}(e)+\mathbf{e}_1]$ or $[\mathbf{x}(e),\ \mathbf{x}(e)-\mathbf{e}_d]$ respectively. We denote it by $\mathbf{W}^1(\mathbf{e}_1)$ or $\mathbf{W}^1(\mathbf{e}_d)$ (Figure 3.6).

Construction of $\mathbf{W}^2$. We concatenate both $\mathbf{W}_1$ and $\mathbf{W}_2$ by L_2 and similarly denote them by $\mathbf{W}_1'$ and $\mathbf{W}_2'$. We define two new walks by

$$\mathbf{W}_i'' = f_{d-1,d}(\mathbf{W}_i), \quad i = 1, 2. \tag{3.53}$$

The new walks are confined to the wedge: $\{x_2 \le 0, \ldots, x_d \le 0, x_{d-1} \ge x_d\}$ and still have $\mathbf{x}^*(n)$ as their end vertex since $x_{d-1}^*(n) = x_d^*(n)$ for $\mathbf{x}^*(n)$. We reflect $\mathbf{W}_2''$ in the hyperplane $x_d = x_d^*(n)$ to get $\mathbf{W}_2'''$ and body shift it by 4 steps in the $\mathbf{e}_d$ direction. We join the two walks $\mathbf{W}_1''$ and $\mathbf{W}_2'''$ by a 4-step walk: $\{\mathbf{x}^*(n),\ \mathbf{x}^*(n)+\mathbf{e}_d,\ \mathbf{x}^*(n)+2\mathbf{e}_d,\ \mathbf{x}^*(n)+3\mathbf{e}_d,\ \mathbf{x}_2''(0)\}$ and obtain another $2(n+d+6)$-step walk. The new walk has its start vertex at $\mathbf{x}(s) = \mathbf{0}$ with the incident edge $[\mathbf{x}(s),\ \mathbf{x}(s)+\mathbf{e}_{d-1}]$ and its end vertex at $\mathbf{x}(e) = (0, \ldots, 0, 2x_d^*(n)+4)$ with the incident edge $[\mathbf{x}(e),\ \mathbf{x}(e)+\mathbf{e}_{d-1}]$. We denote it by $\mathbf{W}^2(\mathbf{e}_{d-1})$ (Figure 3.7).

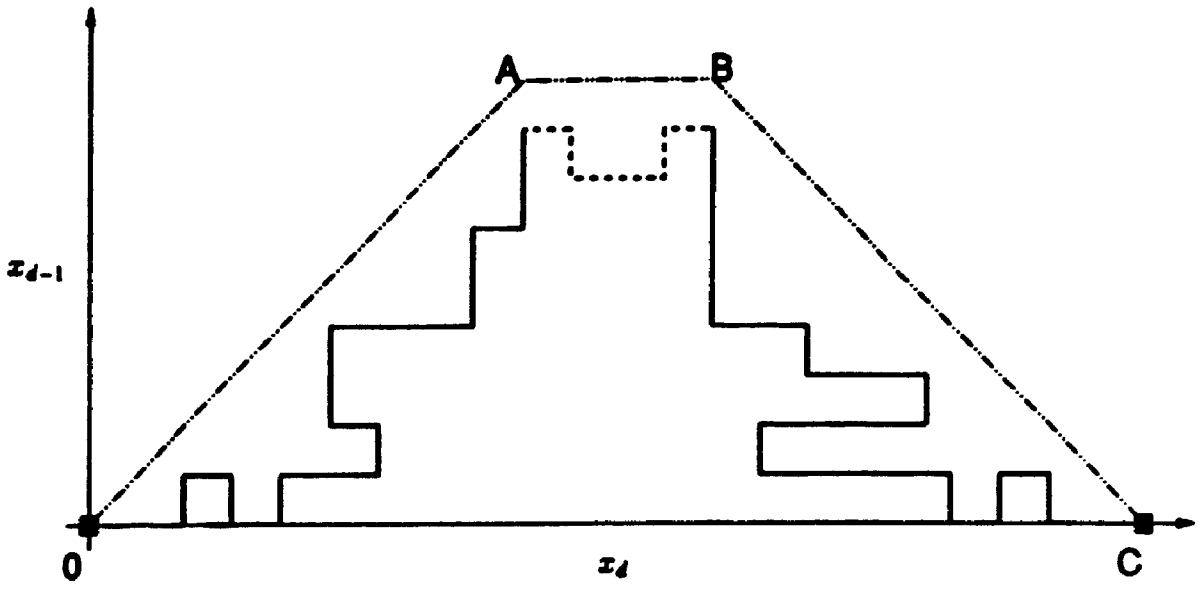


Figure 3.6: Example of the constructed walk $\mathbf{W}^1(\mathbf{e}_d)$. OABC encloses the region $\mathcal{R}$ in (3.54).

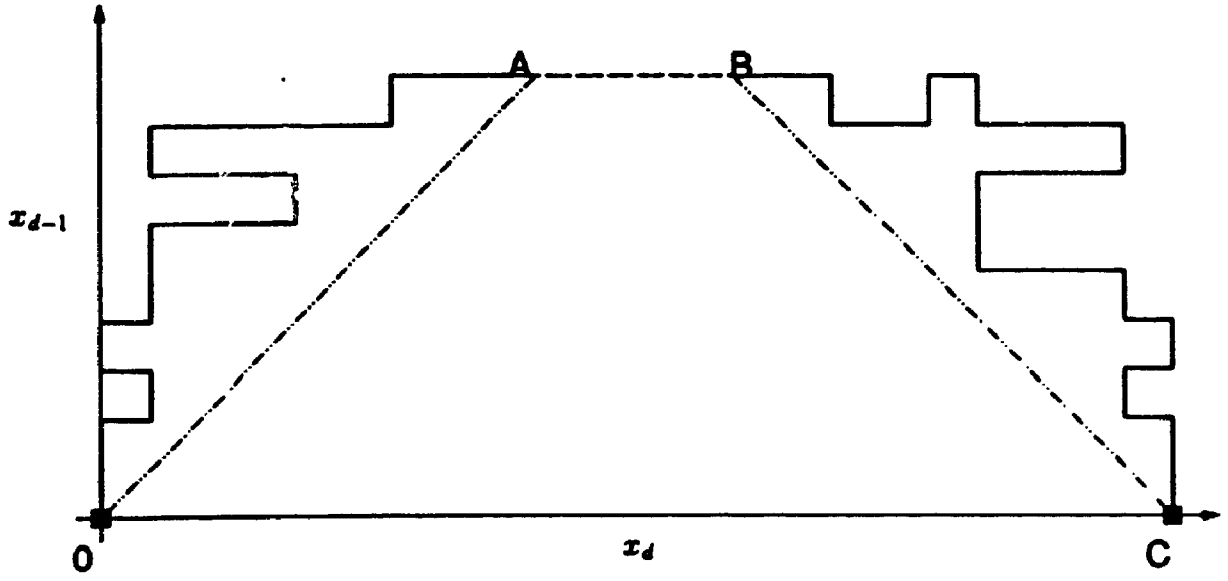


Figure 3.7: Example of showing the joining of two walks $\mathbf{W}_1''$ and $\mathbf{W}_2''''$ by a 4-step walk (dashed line) to form a new walk $\mathbf{W}^2(\mathbf{e}_{d-1})$.

From the contruction, one can see clearly that the walk $\mathbf{W}^1$ is confined in the region,

$$\mathcal{R}: 0 \le x_2, \ \ldots, \ 0 \le x_{d-1} < x_d^*(n), \ x_{d-1} \le x_d \le 2x_d^*(n) + 4 - x_{d-1}, \tag{3.54}$$

while $\mathbf{W}^2$ is confined outside of $\mathcal{R}$ and they only intersect at their start and end vertices (see Figure 3.6 and Figure 3.7). For any two vertices $\mathbf{x}(k_1)$, $\mathbf{x}(k_2)$ in the same walk, we have

$$| x_j(k_1) - x_j(k_2) | \le x_d^*(n) + 1, \quad j \ne d, \tag{3.55}$$

$$| x_d(k_1) - x_d(k_2) | \le 2x_d^*(n) + 4. \tag{3.56}$$

We denote by $\mathcal{W}^i$ the set of all such walks.

The third type component

The third type component is a k-watermelon with $k \le 2(d-1)$, which consists of k chains with their initial vertices being joined together at a single vertex and their terminal vertices being joined together at another single vertex (Figure 1.1 (d)). We give an example to show how to construct a k-watermelon. We take $2k$ walks $\mathbf{W}_1, \ \mathbf{W}_2, \ \ldots, \ \mathbf{W}_{2k}$ from $\mathcal{B}_n^i$. We concatenate $\mathbf{W}_1$ and $\mathbf{W}_2$ by L_1 and the other $2(k-1)$ walks by L_2 and obtain $2k$ new walks $\mathbf{W}_1', \ \ldots, \ \mathbf{W}_{2k}'$. For convenience, we write these $2k$ walks in pairs as

$$\{\mathbf{W}_{2j-1}', \ \mathbf{W}_{2j}'\}, \quad j = 1, \ \ldots, \ k. \tag{3.57}$$

Following the previous constructions, we construct two $2(n+d+6)$-step walks $\mathbf{W}_1^1(\mathbf{e}_1)$, $\mathbf{W}_2^1(\mathbf{e}_d)$ from the first two pairs and $(k-2)$ $2(n+d+6)$-step walks $\mathbf{W}_3^2(\mathbf{e}_{d-1})$, $\ldots$, $\mathbf{W}_k^2(\mathbf{e}_{d-1})$ from the remaining $(k-2)$ pairs. Each of the k new walks has its start vertex at $\mathbf{x}(s) = \mathbf{0}$ and its end vertex at $\mathbf{x}(e) = (0, \ \ldots, \ 2x_d^*(n) + 4)$. All of them are totally confined in the octant:

$$S_1: x_2 \ge 0, \ \ldots, \ x_{d-1} \ge 0, \ x_d \ge 0. \tag{3.58}$$

We leave $\mathbf{W}_1^1(\mathbf{e}_1)$ and $\mathbf{W}_3^2(\mathbf{e}_{d-1})$ in S_1 and apply the composite map $g_{d-1} \cdot f_{d-2,d-1}$ to $\mathbf{W}_2^1(\mathbf{e}_d)$ and $\mathbf{W}_4^2(\mathbf{e}_{d-1})$, which maps the two walks into the octant:

$$S_2 : x_2 \geq 0, \ \ldots, \ x_{d-2} \geq 0, \ x_{d-1} \leq 0, \ x_d \geq 0. \tag{3.59}$$

The new walks have their initial vertices at $\mathbf{x}(s) = \mathbf{0}$ and their terminal vertices at $\mathbf{x}(e) = (0, 0, \ldots, 2x_d^*(n)+4)$ since the coordinates of the vertices are unchanged under the map $g_{d-1} \cdot f_{d-2,d-1}$. The incident edges at the two vertices become $[\mathbf{x}(s), \mathbf{x}(s)+\mathbf{e}_d]$, $[\mathbf{x}(s), \mathbf{x}(s) + \mathbf{e}_{d-2}]$ and $[\mathbf{x}(e), \mathbf{x}(e) - \mathbf{e}_d]$, $[\mathbf{x}(e), \mathbf{x}(e) + \mathbf{e}_{d-2}]$ respectively. For each of the remaining $(k-4)$ walks $\mathbf{W}_5^2(\mathbf{e}_{d-1}), \ \ldots, \ \mathbf{W}_k^2(\mathbf{e}_{d-1})$, we properly choose k'' numbers $i_1 < i_2 < \ldots < i_{k''}$ and another number j from the set $\{2, 3, \ldots, d-1\}$ $(1 \leq k'' \leq d-2)$ and define a composite map by

$$F(i_1, \ \ldots, \ i_{k''}, \ j, \ d-1) = g_{i_1} \cdots g_{i_{k''}} f_{j,d-1}, \tag{3.60}$$

which maps the walk into the octant:

$$S' : x_2 \geq 0, \ \ldots, \ x_{i_1} \leq 0, \ \ldots, \ x_{i_{k''}} \leq 0, \ \ldots, \ x_d \geq 0. \tag{3.61}$$

Similarly, the resulting new walk has the same initial and terminal vertices with the incident edges at the two vertices being $[\mathbf{x}(s), \mathbf{x}(s) + \mathbf{e}_j]$ (or $[\mathbf{x}(s), \mathbf{x}(s) - \mathbf{e}_j]$) and $[\mathbf{x}(e), \mathbf{x}(e) + \mathbf{e}_i]$ (or $[\mathbf{x}(e), \mathbf{x}(e) - \mathbf{e}_j]$). For a hypercubic lattices in d dimensions, there are a total of $2^{d-1} - 2$ such octants defined in (3.61), which is not less than $2(d-1)-4(\geq k-4)$ for $d \geq 3$. Therefore, each of the walks $\mathbf{W}_5^2(\mathbf{e}_{d-1}), \ \ldots, \ \mathbf{W}_k^2(\mathbf{e}_{d-1})$ can be mapped into one individual octant. In this way , all of k $2(n + d + 6)$-step walks intersect only at their first and last vertices and form a vate melon with its two extremes at $\mathbf{x}(s) = \mathbf{0}$ and $\mathbf{x}(e) = (0, \ \ldots, \ 2x_d^*(n) + 4)$ (Figure 3.8).

With a little modification, we can also construct a k-watermelon such that its two extremes $\mathbf{x}(s)$ and $\mathbf{x}(e)$ are on the x_i-axis with $\mathbf{x}(s) = \mathbf{0}$ and $\mathbf{x}(e) = (0, 0, \ldots, 2x_d^*(n)+4, \ \ldots, 0)$. The incident edges at these two vertices are $[\mathbf{0}, \mathbf{e}_i]$, $[\mathbf{0}, \mathbf{e}_{i_2}]$, $\ldots$, $[\mathbf{0}, -\mathbf{e}_{i_k}]$ and $[\mathbf{x}(e), \mathbf{x}(e) - \mathbf{e}_i]$, $[\mathbf{x}(e), \mathbf{x}(e) + \mathbf{e}_{i_2}]$, $\ldots$, $[\mathbf{x}(e), \mathbf{x}(e) - \mathbf{x}_{i_k}]$ respectively. We

denote such a watermelon by $\mathbf{L}(k, \mathbf{e}_i, \mathbf{e}_{i_2}, \ldots, -\mathbf{e}_{i_k})$. Similarly, for any two vertices $\mathbf{x}(k_1)$, $\mathbf{x}(k_2)$ of $\mathbf{L}$, we have

$$| x_j(k_1) - x_j(k_2) | \leq x_d^*(n) + 1, \quad j \neq i, \tag{3.62}$$

$$| x_i(k_1) - x_i(k_2) | \leq 2x_d^*(n) + 4. \tag{3.63}$$

There is a special case of $k = 2$ which is essentially a polygon. For convenience, we refer to it as a 2-watermelon with two uniform $2(n+d+6)$-step branches. We denote by $\mathcal{L}'$ the set of all such watermelons.

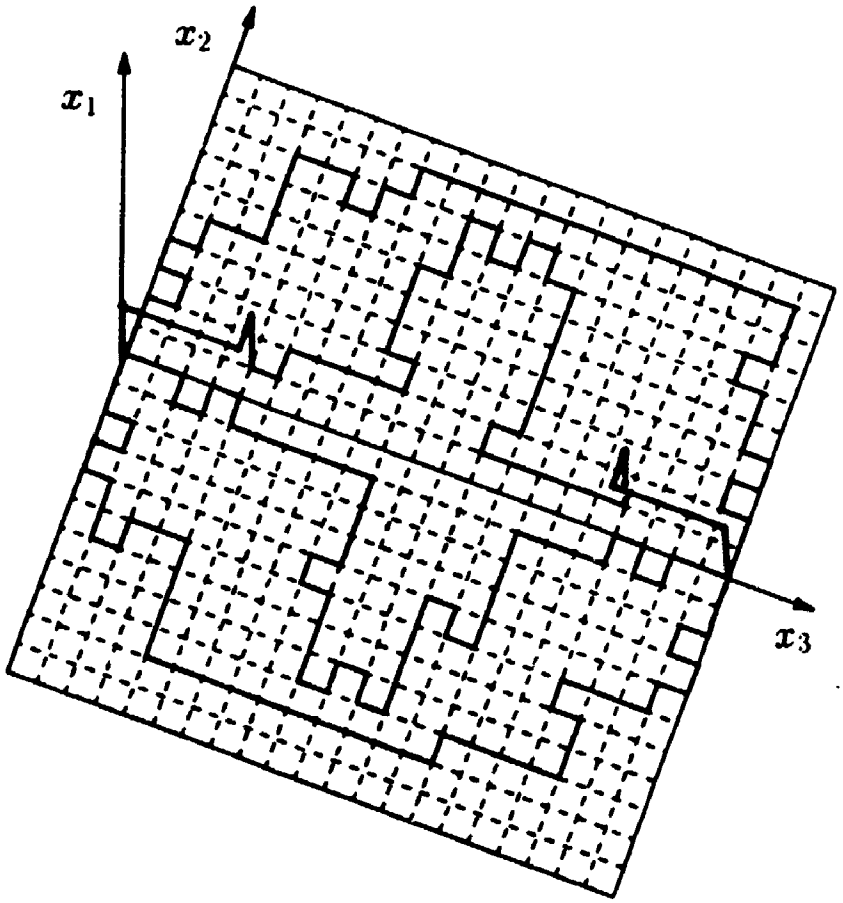


Figure 3.8: Example of a 4-watermelon $\mathbf{L}(4, \mathbf{e}_3, \mathbf{e}_1, \mathbf{e}_2, -\mathbf{e}_2)$ with its two extremes on the x_3-axis, formed by joining the walks $\mathbf{W}_1^1(\mathbf{e}_1)$, $\mathbf{W}_3^2(\mathbf{e}_2)$, $g_2(\mathbf{W}_2^1(\mathbf{e}_3))$ and $g_2(\mathbf{W}_4^2(\mathbf{e}_2))$ in a simple cubic lattice. Under the map $f_{2,3}$, it becomes $\mathbf{L}(4, \mathbf{e}_2, \mathbf{e}_1, -\mathbf{e}_2, \mathbf{e}_3)$ with its two extremes on the x_2-axis.

3.3.3 Precursors for the topology

By using members from $\mathcal{P}^t$, $\mathcal{L}^t$ and $\mathcal{W}^t$, we construct appropriate precursors which are uniform polymer networks with one or no cycles and with the set of vertices $\{b_1', b_3', \ldots, b_{2d}'\}$, where b_i' is minimized such that

$$b_1' = b_1, \tag{3.64}$$

and for $i \geq 3$

$$b_i' \leq b_i. \tag{3.65}$$

There are three such precursors (Gaunt *et al* [13]):

1). For $b_1 = 0$, the precursor is a polygon. We take it as any member of $\mathcal{P}^t$.

2). For $b_1 = 1$, the precursor satisfies

$$b_3' = b_1, \tag{3.66}$$

and for $k > 3$

$$b_k' = 0, \tag{3.67}$$

which indicates that the precursor has one cycle. We take a walk $\mathbf{W}$ from $\mathcal{W}^t$ and a polygon $\mathbf{P}$ from $\mathcal{P}^t$ and join them together at the end vertex of $\mathbf{W}$.

3). For $b_1 \geq 2$, the precursor is a uniform topology with the set of vertices $\{b_1', b_3', \ldots, b_{2d}'\}$ satisfying:

$$\sum_{i=3}^{2d} (i-2)(b_i - b_i') = 2c. \tag{3.68}$$

Such a precursor is obtained as follows. We take two walks $\mathbf{W}_1^1(\mathbf{e}_1)$ and $\mathbf{W}_2^2(\mathbf{e}_{d-1})$ from $\mathcal{W}^t$ and connect them by translating $\mathbf{W}_2^2(\mathbf{e}_{d-1})$ such that its first vertex $\mathbf{x}(s)$ coincides with the last vertex $\mathbf{x}(e)$ of $\mathbf{W}_1^1(\mathbf{e}_1)$. Then from $\mathcal{L}^t$, we take a $(k-2)$-watermelon $\mathbf{L}(k-2, \mathbf{e}_{d-1}, -\mathbf{e}_1, \mathbf{e}_2, -\mathbf{e}_2, \ldots)$ (if $k = 3$, we replace the watermelon by a walk $\mathbf{W}^1(\mathbf{e}_d)$ from $\mathcal{W}^t$, and use the map $f_{d-1,d}$ to let its two end vertices be on the x_{d-1}-axis). We body shift it in the $-\mathbf{e}_{d-1}$ direction to let the extreme $\mathbf{x}(e)$

coincide with the joint of the two walks. We remove the extreme $\mathbf{x}(s)$ and its incident edges, and then add to each branch of $\mathbf{L}$ an edge in the $-\mathbf{e}_{d-1}$ direction, which gives a uniform network with $b_1 = k$ and $b_k = 1$ ($k \leq 2d$). Next, we take $\mathbf{W}_3^1(\mathbf{e}_1)$ from $\mathcal{W}^i$ and $\mathbf{L}'(k'-2, \mathbf{e}_{d-1}, -\mathbf{e}_1, \mathbf{e}_2, -\mathbf{e}_2, \ldots)$ and connect them with $\mathbf{W}_2^2(\mathbf{e}_{d-1})$ at its last vertex $\mathbf{x}(e)$ in the same way. The definitions of the walks and watermelons together with equations (3.55), (3.56), (3.62) and (3.63) ensure that the walks and watermelons are independent of each other. By repeating the procedure, we obtain a uniform topology with the set $\{b_1', \ldots, b_{2d}'\}$. We note that the uniform topology constructed in this way is a uniform brush with the 'backbone' consisting of $\mathbf{W}_1^1(\mathbf{e}_1)$, $\mathbf{W}_2^2(\mathbf{e}_{d-1})$, $\mathbf{W}_3^1(\mathbf{e}_1)$, ... (A brush is a particular tree topology with a self-avoiding 'backbone' formed by branch points of degree ≥ 3 that are connected by n-step SAW's. The topology with all branch points of degree 3 is known as a comb) (Figure 3.9).

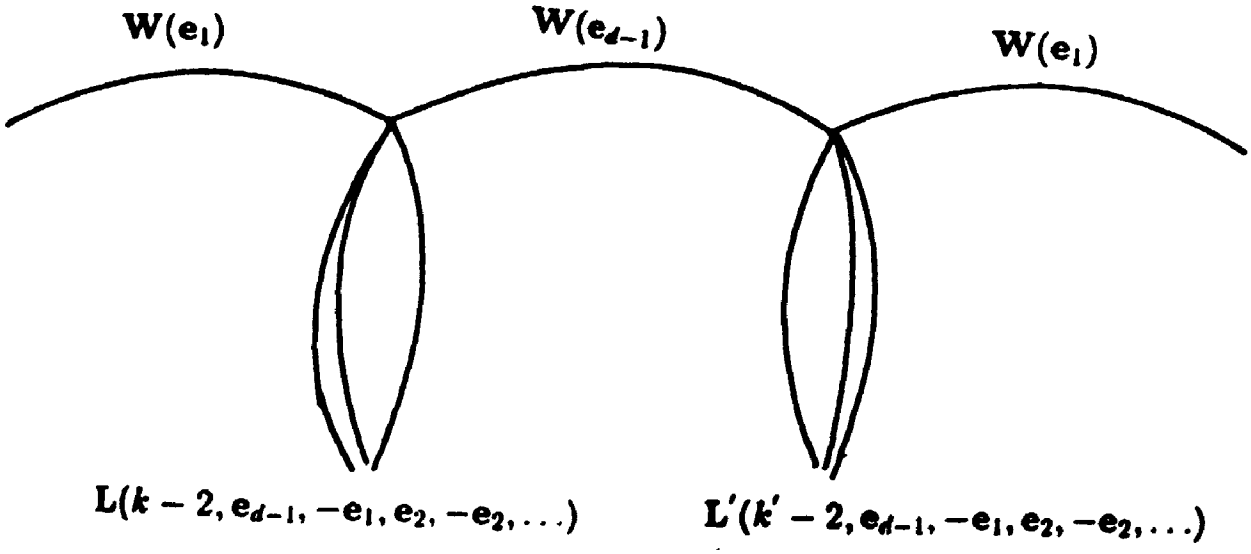


Figure 3.9: The construction of a uniform topology (uniform brushes) as a precursor from walks and watermelons from the sets $\mathcal{W}^i$ and $\mathcal{L}^i$.

3.3.4 A lower bound for the partition function

We now convert the precursors into a uniform network with the set $(c, b_3, \ldots, b_{2d})$ by using the following two constructions. We concentrate on the third case and denote the precursor by $\mathbf{G}'$. In $\mathbf{G}'$, the vertex $\mathbf{x}(s)$ of $\mathbf{W}_1^1(\mathbf{e}_1)$ has degree 1 and satisfies the condition that for any vertex $\mathbf{x}$ of $\mathbf{G}'$, $x_d \geq x_d(s)$. We denote such a vertex by $\mathbf{x}_b$. We start with $\mathbf{x}_b$ of $\mathbf{G}'$, which has the incident edge $[\mathbf{x}_b,\ \mathbf{x}_b + \mathbf{e}_1]$. We will perform all translations as needed in the $-\mathbf{e}_d$ direction:

Construction 1. Adding the vertices of odd degrees to $\mathbf{G}'$. Equation (3.68) implies

$$\sum_{i=1}^{d-1}(b_{2i+1} - b'_{2i+1}) \equiv 0 \pmod 2. \tag{3.69}$$

There remains an even number of such vertices. Starting with the highest degree, we list all of these vertices and write them in pairs. In one such pair, let the first vertex have degree i and the second vertex have degree j, so $i \geq j$ and $i - j = 2k$. We take a $(j-1)$-watermelon $\mathbf{L}(j-1, \mathbf{e}_d, \mathbf{e}_{k_2}, \ldots, -\mathbf{e}_{k_{j-1}})$ from $\mathcal{L}^i$, which has its two extremes on the x_d-axis. We translate it to let its extreme $\mathbf{x}(e)$ coincide with $\mathbf{x}_b$ of $\mathbf{G}'$, which converts $\mathbf{x}_b$ into a vertex of degree j. At the extreme $\mathbf{x}(s)$ of the watermelon, we first join it with the last vertex $\mathbf{x}(e)$ of a walk $\mathbf{W}^1(\mathbf{e}_d)$ from $\mathcal{W}^1$ by translating $\mathbf{W}^1(\mathbf{e}_d)$. We then take k polygons from $\mathcal{P}^1$ such that at $\mathbf{0}$, the incident edges of the polygons are not the edges $[\mathbf{0}, -\mathbf{e}_d], [\mathbf{0}, \mathbf{e}_d], \ldots, [\mathbf{0}, -\mathbf{e}_{k_{j-1}}]$, and by a translation, the polygons are confined in k of the remaining $2^{d-2} - 1$ octants which satisfy $x_d \leq x_d(s)$ at $\mathbf{x}(s)$ of the watermelon. By joining the polygons in this way, we convert the extreme $\mathbf{x}(s)$ into a vertex of degree i. Thus, we add the precursor with a vertex of degree i and a vertex of degree j, which produces $[1 + (i + j - 6)/2]$ cycles. We repeat the procedure for all pairs and obtain a uniform polymer network $\mathbf{G}''$ with b_{2i+1} of vertices with degree $2i+1$. The vertex $\mathbf{x}(s)$ of the last walk added becomes $\mathbf{x}_b$ of $\mathbf{G}''$ with incident edge $[\mathbf{x}_b,\ \mathbf{x}_b + \mathbf{e}_d]$.

Construction 2. Adding a vertex of degree $2k$ (forming $(k-1)$ cycles) to $\mathbf{G}''$. We first join $\mathbf{x}_b$ of $\mathbf{G}''$ by a walk $\mathbf{W}_1^2(\mathbf{e}_{d-1})$ from $\mathcal{W}^i$ to convert it into a vertex of degree 2 with incident edges $[\mathbf{x}_b,\ \mathbf{x}_b+\mathbf{e}_{d-1}]$ and $[\mathbf{x}_b,\ \mathbf{x}_b+\mathbf{e}_d]$. We then take $k-1$ polygons from $\mathcal{P}^i$, which, at $\mathbf{0}$, have incident edges other than $[\mathbf{0},\ \mathbf{e}_{d-1}]$ and $[\mathbf{0},\ \mathbf{e}_d]$, and can be translated to be confined in the other 2^{d-2} octants at $\mathbf{x}_b$. By joining the $k-1$ polygons at the joint vertex $\mathbf{x}_b$, we have thus added a vertex of degree $2k$ and $k-1$ cycles to $\mathbf{G}''$. The new $\mathbf{x}_b$ is the vertex $\mathbf{x}(s)$ of $\mathbf{W}_1^2(\mathbf{e}_{d-1})$ with incident edge $[\mathbf{x}_b,\ \mathbf{x}_b+\mathbf{e}_{d-1}]$. Next, we take a walk $\mathbf{W}_2^1(\mathbf{e}_d)$ from $\mathcal{W}^i$ and $k'-1$ polygons and add them to $\mathbf{x}_b$ to convert it into a vertex of degree $2k'$, which yields $k'-1$ cycles. The procedure is repeated until all needed vertices of even degree have been added.

This procedure yields a uniform polymer network $\mathbf{G}_{2(n+d+6)}(c, b_3, \ldots, b_{2d})$ with each of its chains being constructed from 2 members of $\mathcal{B}_n^i$ and having a length of $2(n+d+6)$-step. Similarly, based on the above constructions, we can convert the other two precursors into a polymer network.

Generally, we take a group of $2K$ walks $\mathbf{W}_1,\ \mathbf{W}_2,\ \ldots,\ \mathbf{W}_{2K}$ from $\mathcal{B}_n^i$ such that $\mathbf{W}_i$ has m_i+1 vertices in the surface $x_1=0$. We first concatenate K_1 of the walks with L_1 and the rest of K_2 walks with L_2, where $2K=K_1+K_2$, and then use these walks to construct the required walks, watermelons and polygons. By following the above procedure to join these components together, we obtain a polymer network $\mathbf{G}_{2(n+d+6)}(c, b_3, \ldots, b_{2d})$. Since, L_1 has two vertices and L_2 has $d+5$ vertices in the surface respectively, the resulting network $\mathbf{G}$ can have either $m+K_1+K_2(d+5)-b^*+1$ or $m+K_1+K_2(d+5)-b^*+1+4K$ vertices in the surface, depending on the position of the end vertex $\mathbf{x}^*(n)$ of the walks, where $m=m_1+\cdots+m_{2K}$ and $b^*=\sum_{i\neq 2} b_i$. The construction of $\mathbf{G}_{2(n+d+6)}(c, b_3, \ldots, b_{2d})$ from the walks $\mathbf{W}_1,\ \ldots,\ \mathbf{W}_{2K}$ is considered as a standard procedure which has to be followed whenever a group of $2K$ walks from $\mathcal{B}_n^i$ are used to construct a polymer network. Hence, a distinct group of $2K$ walks

will give a distinct polymer network $\mathbf{G}_{2(n+d+6)}(c, b_3, \ldots, b_{2d})$. We denote by $b^i_{n,m}$ the number of walks in the ith subclass with $m+1$ vertices in the surface. We obtain

$$\prod_{j=1}^{2k} b^i_{n,m_j} \leq g_{N,m+K_1+K_2(d+5)-b^*} + g_{N,m+K_1+K_2(d+5)-b^*+4K} \tag{3.70}$$

with $m = m_1 + m_2 + \ldots + m_{2K}$ and $N = 2K(n+d+6) - c + 1$. We write

$$B_n(\omega, i) = \sum_{m=0}^{n} b^i_{n,m} e^{m\omega} \tag{3.71}$$

as the partition function for walks in the ith subclass. From (3.70) we have

$$\begin{aligned}
[B_n(\omega,i)]^{2K} &= \left(\sum_{m=0}^{n} b^i_{n,m} e^{m\omega}\right)^{2K} \\
&= \sum_{0\leq m_1+m_2+\ldots+m_{2K}\leq 2Kn} \prod_{j=1}^{2K} b^i_{n,m_j} e^{m\omega} \\
&\leq \sum_{0\leq m_1+m_2+\ldots+m_{2K}\leq 2Kn} \\
&\quad (g_{N,m+K_1+K_2(d+5)-b^*} + g_{N,m+K_1+K_2(d+5)-b^*+4K}) e^{m\omega} \\
&\leq (2Kn)^{2K} f(\omega) G_N(c, n_3, \ldots, n_{2d}, \omega),
\end{aligned} \tag{3.72}$$

where $f(\omega) = (1+e^{4k|\omega|})e^{[K_1+K_2(d+5)-b^*]|\omega|}$. Let $p = 2K$ and $q = 2K(2K-1)^{-1}$, then $p^{-1} + q^{-1} = (2K)^{-1} + (2K-1)(2K)^{-1} = 1$. By Hölder's inequality, we have

$$\begin{aligned}
[B_n(\omega)]^{2K} &= \left(\sum_{i=1}^{I} B_n(\omega, i)\right)^{2K} \\
&\leq \left(\sum_{i=1}^{I} 1^{2K/(2K-1)}\right)^{2K-1} \sum_{i=1}^{I} (B_n(\omega,i))^{2K} \\
&\leq I^{2K+1}(2Kn)^{2K} f(\omega) G_N(c, n_3, .., n_{2d}, \omega).
\end{aligned} \tag{3.73}$$

Combining it with (3.26) establishes

$$A(\omega) \leq \lim_{n\to\infty} \inf \frac{1}{N} \ln G_N(c, b_3, \ldots, b_{2d}, \omega) \tag{3.74}$$

for even n.

3.3.5 An upper bound for the partition function

We derive an upper bound on the partition function $G_N(c, b_3, \ldots, b_{2d}, \omega)$ regardless of whether n is even or odd.

We classify all networks by the number of branches which have at least on vertex in the surface. There are K such classes. For a network in each class, if a branch of the network has vertices in the surface, we choose one of these vertices and consider this branch as a nonuniform 2-star rooted on the surface at the chosen vertex. For a branch without any vertex in the surface, we consider it as a self-avoiding walk in the bulk. We denote by $G_N(c, b_1, \ldots, b_{2d}, \omega, k)$ the partition function for networks in the kth class. By treating each branch independently, we obtain

$$G_N(c, b_1, \ldots, b_{2d}, \omega, k) \le T(b^*)[S_n(2,\omega)]^k (a_n)^{K-k}, \tag{3.75}$$

where a_n is the number of n-step walks in the bulk, $S_n(2,\omega)$ is defined by (2.30), and $T(b^*)$ is the number of ways of connecting the set $\{b_1, b_3, \ldots, b_{2d}\}$ with $b^* = b_1 + b_3 + \cdots + b_{2d}$. From Gaunt *et al* [13], $T(b^*) \le 2^{b^*(b^*-1)/2}$. From (1.5), (2.5) and (2.32), we have, for a given ω,

$$S_n(2,\omega) \le e^{nA(\omega)+o(n)}, \tag{3.76}$$

$$a_n \le e^{n\kappa+o(n)} \le e^{nA(\omega)+o(n)}, \tag{3.77}$$

Substituting them in (3.75) yields

$$G_N(c, b_1, \ldots, b_{2d}, \omega, k) \le 2^{b^*(b^*-1)/2} e^{KnA(\omega)+o(n)}. \tag{3.78}$$

Therefore, we have

$$\begin{aligned} G_N(c, b_3, \ldots, b_{2d}, \omega) &= \sum_k^K G_N(c, b_3, \ldots, b_{2d}, \omega, k) \\ &\le K 2^{b^*(b^*-1)/2} e^{KnA(\omega)+o(n)}, \end{aligned} \tag{3.79}$$

and

$$\limsup_{n\to\infty} \frac{1}{N} \ln G_N(c, b_1, \ldots, b_{2d}, \omega) \le A(\omega). \tag{3.80}$$

Combining it with (3.74) gives (3.20).

3.3.6 The adsorption of networks at an impenetrable surface

When the interaction surface is impenetrable, a network is then totally confined to one side of the surface, say $x_1 \geq 0$. In this case, we consider the set $\mathcal{B}_n^+$, which is the subset of $\mathcal{B}_n$ satisfying

$$x_1(i) \geq 0 \qquad i = 0, 1, \ldots, n. \tag{3.81}$$

By following the same procedure in lemma 3.1, we can show that

$$\lim_{n\to\infty} \frac{1}{n} \ln B_n^+(\omega) = A^+(\omega). \tag{3.82}$$

where $B_n^+(\omega)$ is the corresponding partition function for walks in the set $\mathcal{B}_n^+$.

By the previous procedure, the constructed network has all its b_i ($i \neq 2$) vertices of degree i in the adsorption surface $x_1 = 0$. When the surface is impenetrable, a branch point of degree $2d$ can not locate on the surface. To avoid it, we replace the two links L_1 and L_2 by three new uniform finite step walks L_1', L_2' and L_3' defined by

$$\begin{aligned} L_1' = \{&3\mathbf{e}_1,\ 2\mathbf{e}_1,\ 2\mathbf{e}_1+\mathbf{e}_d,\ \mathbf{e}_1+\mathbf{e}_d,\ \mathbf{e}_1,\ \mathbf{0},\ \mathbf{e}_d,\ 2\mathbf{e}_d,\ 3\mathbf{e}_d,\ \mathbf{e}_{d-1}+3\mathbf{e}_d,\\ &\ldots,\ \mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+3\mathbf{e}_d,\ \mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+4\mathbf{e}_d\}; \end{aligned} \tag{3.83}$$

$$\begin{aligned} L_2' = \{&3\mathbf{e}_1,\ 3\mathbf{e}_1+\mathbf{e}_d,\ 3\mathbf{e}_1+2\mathbf{e}_d,\ 2\mathbf{e}_1+2\mathbf{e}_d,\ 2\mathbf{e}_1+3\mathbf{e}_d,\ 3\mathbf{e}_1+3\mathbf{e}_d,\\ &3\mathbf{e}_1+4\mathbf{e}_d,\ 2\mathbf{e}_1+4\mathbf{e}_d\ldots,\ \mathbf{e}_1+4\mathbf{e}_d,\ 4\mathbf{e}_d,\ \mathbf{e}_{d-1}+44_d,\ \ldots,\\ &\mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+4\mathbf{e}_d\}; \end{aligned} \tag{3.84}$$

$$\begin{aligned} L_3' = \{&3\mathbf{e}_1,\ 4\mathbf{e}_1,\ 4\mathbf{e}_1+\mathbf{e}_d,\ \ldots,\ 4\mathbf{e}_1+4\mathbf{e}_d,\ 4\mathbf{e}_1+\mathbf{e}_{d-1}+4\mathbf{e}_d,\ \ldots,\\ &4\mathbf{e}_1+\mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+4\mathbf{e}_d,\ \ldots,\ 3\mathbf{e}_1+\mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+4\mathbf{e}_d,\\ &\ldots,\ \mathbf{e}_2+\cdots+\mathbf{e}_{d-1}+4\mathbf{e}_d\}. \end{aligned} \tag{3.85}$$

They are confined to $x_1 \geq 0$ and only intersect at the vertices $\mathbf{A} = (3, 0, \ldots, 0)$ and $\mathbf{x}(0) = \mathbf{e}_2 + \cdots + \mathbf{e}_{d-1} + 4\mathbf{e}_d$. The first step of L_1' is the edge $[\mathbf{A},\ \mathbf{A} - \mathbf{e}_1]$, and the

first step of L_2' is the edge $[\mathbf{A},\ \mathbf{A}+\mathbf{e}_1]$ and the first step of L_3' is the edge $[\mathbf{A},\ \mathbf{A}+\mathbf{e}_1]$ (Figure 3.10).

By concatenating the walks in $\mathcal{B}_n^+$ with the three new links and following the same procedures as in section 3.3.2, we can construct the corresponding polygons, walks and watermelons. All of these new components will have their $\mathbf{x}(s)$'s and $\mathbf{x}(e)$'s in the surface $x_1 = 3$. Then by using these new components and following the same procedure in section 3.3.3 and section 3.3.5, but replacing $A(\omega)$ with $A^+(\omega)$ where neccessary, we obtain that

$$\lim_{n\to\infty} \frac{1}{N} \ln G_N^+(c, b_3, \ldots, b_{2d}, \omega) = A^+(\omega). \tag{3.86}$$

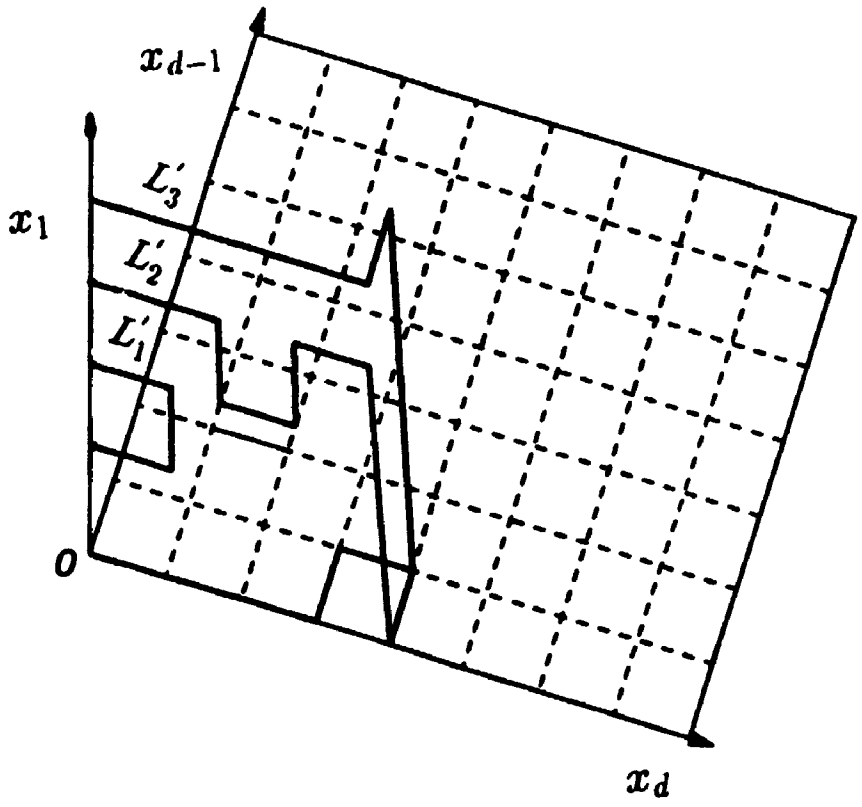


Figure 3.10: Three new finite walks L_1', L_2' and L_3' defined by (3.83)-(3.85).

3.4 Uniform networks interacting with a surface: $d = 2$

In the section 3.3, we have shown that, for $d \geq 3$, the reduced free energy for uniform networks interacting with a $(d-1)$-dimensional surface is independent of the topology which is specified by the set $\{c, b_3, \ldots, b_{2d}\}$. However, for $d = 2$, the conclusion does not hold. For instance, consider a uniform 3-star in the square lattice, interacting with an impenetrable surface. If we denote by $S_n(3,\omega)$ the partition function for such 3-stars, it has been shown by Whittington and Soteros [56] that

$$\begin{aligned} \max\{\kappa,\ (\kappa + 2\omega)/3\} &\leq \lim_{n\to\infty} \inf \frac{1}{3n} \ln S_n(3,\omega) \\ &\leq \lim_{n\to\infty} \sup \frac{1}{3n} \ln S_n(3,\omega) \leq \min\{\kappa + 2\omega/3,\ A^+(\omega)\}. \end{aligned} \tag{3.87}$$

These inequalities indicate that if the reduced free energy exists for 3-stars, it is a non-analytic function of ω and hence there exists a transition point which is at least as low as that for self-avoiding walks; also for large enough ω, the reduced free energy is different from $A^+(\omega)$.

These results can be improved by showing that if the reduced free energy exists for 3-stars, it has the same transition point and the same crossover behaviour at this point as that for walks. In the following we outline a proof. For convenience, we do not distinguish the surface and denote the reduced free energy simply by $A(\omega)$. In the square lattice, a vertex is represented by $(x,\ y)$.

We start with the walks in the set C_n defined by (2.35) and (2.36) in section 2.1.3. For each walk in C_n, we translate it by one step in the positive y direction and add one edge to connect its start vertex with the origin, which yields a new walk which satisfies that $x(0) < x(i)$ for any i. From (2.40), the new walks have the same reduced free energy $A(\omega)$. At the origin 0, we define two wedges by : $\mathcal{W}_1$: $\{(x,\ y),\ 0 \leq x < -y\}$, $\mathcal{W}$: $\{(x,\ y),\ -x < y \leq 0\}$. We denote by $\mathcal{B}'_n$ and $\mathcal{B}''_n$ the set of n-step walks which start at 0 and are confined in $\mathcal{W}_1$ and $\mathcal{W}_2$ respectively and let

b'_n and b''_n be the number of walks in these two sets. It has been shown (Hammersley and Whittington [55]) that

$$\lim_{n\to\infty} \frac{1}{n} \ln b'_n = \lim_{n\to\infty} \frac{1}{n} \ln b''_n = \kappa. \tag{3.88}$$

By taking a walk from each set, we obtain a uniform 3-star. Any distinct such triplet gives a distinct 3-star. Therefore, we have

$$b'_n b''_n C_n(\omega) \leq S_n(3,\omega). \tag{3.89}$$

Taking logarithm and dividing by $3n$ and letting $n \to \infty$ yields

$$\kappa/2 + A(\omega)/3 \leq \liminf_{n\to\infty} \frac{1}{3n} \ln S_n(3,\omega). \tag{3.90}$$

Combining it with (3.87), we obtain that if the limit

$$\lim_{n\to\infty} \frac{1}{3n} \ln S_n(3,\omega) = S(3,\omega) \tag{3.91}$$

exists, then

$$\kappa/2 + A(\omega)/3 \leq S(3,\omega) \leq A(\omega). \tag{3.92}$$

This equation shows that $S(3,\omega)$ has the same transition point as that for $A(\omega)$. Also for $\omega > \omega_c$, from (2.6) and (3.92), we have

$$\frac{1}{3}[A(\omega) - A(\omega_c)] \leq S(3,\omega) - S(3,\omega_c) \leq A(\omega) - A(\omega_c). \tag{3.93}$$

, Taking logarithm, dividing by $\ln(\omega - \omega_c)$ and letting $\omega \to \omega_c$ yields, from (2.8)

$$1/\phi \leq \lim_{\omega\to\omega_c} \frac{\ln[S(3,\omega) - S(3,\omega_c)]}{\ln(\omega - \omega_c)} \leq 1/\phi \tag{3.94}$$

which implies that $S(3,\omega)$ has the same crossover exponent ϕ as that for $A(\omega)$. Therefore, they have the same crossover behaviour at ω_c.

If, for each walk of C_n, we also define two wedges at its end vertex and concatenate it at the end vertex with two walks which are confined in defined two wedges, we obtain

a uniform a uniform H-comb. By following the same arguments, we can show that

$$\begin{aligned} \kappa/4 + A(\omega)/5 &\leq \lim_{n\to\infty} \inf \frac{1}{5n} \ln H_n(\omega) \\ &\leq \lim_{n\to\infty} \sup \frac{1}{5n} \ln H_n(\omega) \leq A(\omega). \end{aligned} \tag{3.95}$$

which, in turn, shows that H-combs have the same ω_c and ϕ as that for walks.

From these two examples, we may suggest that in the two dimensional lattice, for uniform polymer networks with a general topology, the transition point and crossover exponent are the same as that for self-avoiding walks. However, we have not been able to extend the same results to polymer networks with other topologies, for instance, polygons in the two dimensional lattice.

3.5 The adsorption of nonuniform polymer networks

One can also consider the interaction between an adsorption surface and nonuniform polymer networks with the set $\{c, b_3, \ldots, b_{2d}\}$ and a total number of n vertices. By following an analogous procedure, we can show that for $d \geq 3$, the reduced free energies $A(\omega)$ and $A^+(\omega)$ are independent of the topology. For networks in a two dimensional lattice, such results can only be obtained for networks with $n_1 \neq 0$.

In the following, we consider the networks which have the third kind of precursors for $d \geq 2$, regardless of the type of the surface. We outline a proof analogous to that given in section 3.3.3 and section 3.3.4.

We take a walk $\mathbf{W}$ from $\mathcal{C}_n$ (or $\mathcal{C}_n^+$) defined by (2.35) and (2.36) in section 2.1.3 and concatenate it with a finite step walk $\{\mathbf{x}(n), \mathbf{x}(n) + \mathbf{e}_1, \mathbf{x}(n) + 2\mathbf{e}_1, \mathbf{x}(n) + 3\mathbf{e}_1, \mathbf{x}(n) + 3\mathbf{e}_1 + \mathbf{e}_d\}$. This gives an $n + 4$-step walk which has the same number of vertices in the surface $x_1 = 0$ as $\mathbf{W}$. For the new walk, its last vertex has its x_d coordinate strictly greater than any other vertices. We denote such a vertex by $\mathbf{x}_t$. We add $(k-1)$ edges $[\mathbf{x}_t, \mathbf{x}_t + \mathbf{e}_d]$, $[\mathbf{x}_t, \mathbf{x}_t + \mathbf{e}_{d-1}]$, $[\mathbf{x}_t, \mathbf{x}_t - \mathbf{e}_{d-1}]$, ..., to $\mathbf{x}_t$ which

converts it into a vertex of degree k and converts the walk into a topology with $b_1 = k$ and $b_k = 1$. Next, we repeat the same procedure at the vertex $\mathbf{x}_t + \mathbf{e}_d$ and convert it into a vertex of degree k' and so on. Finally, we obtain a nonuniform precursor $\mathbf{G}_1$ with the set of vertices $\{b_1, b_3', \ldots, b_{2d}'\}$.

Analogous to construction 1, we first add to $\mathbf{x}_t$ of $\mathbf{G}_1$ two vertices $\mathbf{x}_t' = \mathbf{x}_t + \mathbf{e}_d$ and $\mathbf{x}'' = \mathbf{x}_t' + \mathbf{e}_d$ and the edges $[\mathbf{x}_t, \mathbf{x}_t']$ and $[\mathbf{x}_t', \mathbf{x}_t'']$. We then add $(j-1)$ 3-step walks: $\{\mathbf{x}_t, \mathbf{x}_t + \mathbf{e}_{d-1}, \mathbf{x}_t + \mathbf{e}_{d-1} + \mathbf{e}_d, \mathbf{x}_t'\}$, $\{\mathbf{x}_t, \mathbf{x}_t - \mathbf{e}_{d-1}, \mathbf{x}_t - \mathbf{e}_{d-1} + \mathbf{e}_d, \mathbf{x}_t'\}$, ..., which converts $\mathbf{x}_t$ and $\mathbf{x}_t'$ into two vertices of degree j. Then at $\mathbf{x}_t$, we add $k = (i-j)/2$ 4-cycles: $\{\mathbf{x}_t, \mathbf{x}_t + \mathbf{e}_1, \mathbf{x}_t + \mathbf{e}_1 + \mathbf{e}_2, \mathbf{x}_t + \mathbf{e}_2, \mathbf{x}_t\}$, $\{\mathbf{x}_t, \mathbf{x}_t - \mathbf{e}_1, \mathbf{x}_t - \mathbf{e}_1 - \mathbf{e}_2, \mathbf{x}_t - \mathbf{e}_2, \mathbf{x}_t\}$, and so on. Next, we repeat the same procedure at the vertex $\mathbf{x}_t''$. By this process, we obtain a network $\mathbf{G}_2$ which has b_{2i+1} vertices of degree $2i+1$.

Analogous to construction 2, we add to $\mathbf{x}_t$ of $\mathbf{G}_2$ a 3-step walk $\{\mathbf{x}_t + \mathbf{e}_{d-1}, \mathbf{x}_t + \mathbf{e}_{d-1} + \mathbf{e}_d, \mathbf{x}_t + \mathbf{e}_{d-1} + 2\mathbf{e}_d\}$, which converts $\mathbf{x}_t$ into a vertex of degree 2. At $\mathbf{x}_t$, we add $(k-1)$ 4-cycles: $\{\mathbf{x}_t, \mathbf{x}_t - \mathbf{e}_{d-1}, \mathbf{x}_t - \mathbf{e}_{d-1} + \mathbf{e}_{d-2}, \mathbf{x}_t + \mathbf{e}_{d-2}, \mathbf{x}_t\}$, $\{\mathbf{x}_t, \mathbf{x}_t - \mathbf{e}_{d-2}, \mathbf{x}_t - \mathbf{e}_{d-2} + \mathbf{e}_{d-3}, \mathbf{x}_t + \mathbf{e}_{d-3}, \mathbf{x}_t\}$, ..., which converts $\mathbf{x}_t$ into a vertex of degree $2k$. We repeat the same procedure at the vertex $\mathbf{x}_t + \mathbf{e}_{d-1} + 2\mathbf{e}_d$ and so on until all needed vertices of even degree have been added.

During this process, a finite number of vertices have been added and none of them is in the surface. Each walk in $C_{n'}$ gives a distinct topology $\mathbf{G}$ with n vertices, b_3 of degree 3, ..., b_{2d} of degree $2d$, c cycles and the same number of vertices in the surface. Therefore, denoting by G_n' the partition function for such networks, we have

$$G_n'(c, b_3, \ldots, b_{2d}, \omega) \geq C_{n'}(\omega). \tag{3.96}$$

From (2.40), we obatin that

$$\liminf_{n\to\infty} \frac{1}{n} \ln G_n'(c, b_3, \ldots, b_{2d}, \omega) = A(\omega) \tag{3.97}$$

for any n. By following the same arguments in section 3.3.5, we can also establish

$$G_n'(c, b_3, \ldots, b_{2d}, \omega) \leq C e^{nA(\omega)+o(n)} \tag{3.98}$$

for some constant C. Then from (3.97) and (3.98)

$$\lim_{n\to\infty} \frac{1}{n} \ln G'_n(c, b_3, \ldots, b_{2d}, \omega) = A(\omega). \tag{3.99}$$

3.6 Conclusions

We have studied the interaction between a surface and polymer networks with a specific topology defined by the values $\{c,\ b_3,\ \ldots,\ b_{3d}\}$. Our rigorous results for $d \geq 3$ and examples for $d = 2$ indicate that for such networks, the transition points and crossover exponents are exactly the same as that for SAW's and therefore, independent of the topology. In section 2.2, we have mentioned that for SAW's interacting with a penetrable surface, scaling theory predicts that $\phi = 1 - \nu$ (Bray and Moore [45]). If such a scaling form also holds for networks interacting with a penetrable surface, our results show that ν is the same for SAW's and polymer networks.

Chapter 4

Randomly Branched Polymers: Lattice Animals

4.1 Preliminary

Although lattice animals had been previously studied in the mathematical literature (Klarner [58]), they were first seriously considered as a model for branched polymers by Lubensky and Isaacson [18]. They proposed a field theory showing that the lattice animals can be considered as models for randomly branched polymers with excluded-volume effects in dilute solution in much the same way that self-avoiding walks have been used as models of linear polymers with excluded volume. The configuration properties of lattice animals in the bulk have been discussed in chapter 1.

In this chapter, we study the interaction of an adsorption surface with lattice animals, which can be considered as a model for the study of the adsorption of randomly branched polymers. In section 4.2, we consider the adsorption of bond trees, bond animals and site animals and show that results analogous to (2.3)-(2.9) for walks can also be established for these models with κ and κ' being replaced by the corresponding growth connective constants. In section 4.3 and section 4.4, we generalize the results (1.18) and (1.20) for bond c-animals to the case where an adsorption surface exists. In section 4.5, we consider a special case for the adsorption of site trees and site c-animals. Section 4.6 gives numerical results. Aspects of the

work included here has been published in Lookman *et al* [59] and Zhao and Lookman [60].

For convenience, we represent a vertex by $\mathbf{v} = (x_1, \ldots, x_d)$. For each embedding, we denote by $\mathcal{V}$, $\mathcal{E}$ the vertex set and the edge set of the embedding respectively. We shall need the following definitions and theorems.

The *top* (*bottom*) vertex of $\mathcal{V}$ is defined as follows. First construct the subset $\mathcal{V}_1$ such that the coordinate x_1 of every vertex in $\mathcal{V}_1$ has the maximum (minimum) value over all vertices in $\mathcal{V}$. We then recursively construct $\mathcal{V}_k \subset \mathcal{V}_{k-1}$ such that the coordinate x_k of every vertex in $\mathcal{V}_k$ has the maximum (minimum) value over all vertices in $\mathcal{V}_{k-1}$, Let j be the smallest integer such that $\mathcal{V}_j$ contains precisely one vertex, and call this vertex $\mathbf{v}_t$ ($\mathbf{v}_b$) the top (bottom) vertex of $\mathcal{V}$. In the same way, we can define the *top* (*bottom*) vertex for a subset of $\mathcal{V}$.

The *top* edge of $\mathcal{E}$ is defined as follows. All vertices which are directly connected to the top vertex $\mathbf{v}_t$ form a subset of $\mathcal{V}$. We can define the top vertex $\mathbf{v}_t'$ for this subset. The top edge is the edge which connects $\mathbf{v}_t$ and $\mathbf{v}_t'$.

The *distance* between two vertices $\mathbf{v}_1 = (x_1, \ldots, x_d)$ and $\mathbf{v}_2 = (y_1, \ldots, y_d)$ is defined as

$$d(\mathbf{v}_1, \mathbf{v}_2) = \sum_{i=1}^{d} | x_i - y_i |, \tag{4.1}$$

which essentially is the minimum number of steps needed to connect two vertices in the lattice.

The *nearest neighbour vertex* of a vertex $\mathbf{v}$ is the vertex which is one step apart from $\mathbf{v}$. The set formed by all such vertices is the *nearest neighbourhood* of $\mathbf{v}$.

Any two vertices which are one step apart and are not connected with each other form a *contact*.

The *distance* of two vertex sets $\mathcal{V}_1$ and $\mathcal{V}_2$ is defined as

$$d(\mathcal{V}_1, \mathcal{V}_2) = \inf_{\mathbf{v}_1 \in \mathcal{V}_1,\ \mathbf{v}_2 \in \mathcal{V}_2} d(\mathbf{v}_1, \mathbf{v}_2). \tag{4.2}$$

The following theorem immediately follows.

Theorem 4.1 *For any finite sets $\mathcal{V}_1$ and $\mathcal{V}_2$, there exist $\mathbf{v}_1' \in \mathcal{V}_1$ and $\mathbf{v}_2' \in \mathcal{V}_2$ such that*

$$d(\mathcal{V}_1, \mathcal{V}_2) = d(\mathbf{v}_1', \mathbf{v}_2'). \tag{4.3}$$

The following theorems and corollary will be used quite often in establishing limits in the following sections.

Theorem 4.2 (Hammersley [61]) *Suppose a_n is a sequence such that a_n/n is bounded below and*

$$a_{n+m} \leq a_n + a_m + b_{n+m} \tag{4.4}$$

for $n,\ m \geq N$, where N is a constant and b_n is a non-decreasing sequence. Then there exists a constant μ such that

$$\lim_{n\to\infty} \frac{1}{n} \ln a_n = \ln \mu \tag{4.5}$$

iff the series $\sum_{n\geq N} b_n/n^2$ is convergent.

Theorem 4.3 (Wilk and Whittington [62]) *Suppose a_n is a non-decreasing sequence of positive numbers such that $n^{-1} \ln a_n$ is bounded above and*

$$a_n a_m \leq a_{n+f(m)} \tag{4.6}$$

for some positive function f which satisfies

$$\lim_{m\to\infty} \frac{f(m)}{m} = 1. \tag{4.7}$$

Then there exists a positive constant μ such that

$$\lim_{n\to\infty} \frac{1}{n} \ln a_n = \ln \mu. \tag{4.8}$$

Corollary 4.1 *Let a_n be the sequence given in theorem 4.3, except it satisfies*

$$a_n a_m \leq C a_{n+f(m)}, \tag{4.9}$$

where C is a positive constant. Then the limit

$$\lim_{n\to\infty} \frac{1}{n} \ln a_n = \ln \mu \tag{4.10}$$

exists.

Proof: The prove is simple. We let $b_n = a_n/C$. One can verify that b_n is non-decreasing , $n^{-1} \ln b_n = n^{-1}(\ln a_n - C)$ is bounded, and from (4.9), it satisfies

$$b_n b_m = a_n a_m / C^2 \leq C a_{n+f(m)}/C^2 = b_{n+f(m)}. \tag{4.11}$$

From theorem 4.3, we obtain (4.10).

4.2 The adsorption of randomly branched polymers

In this section, we consider the interaction of an adsorption surface at $x_1 = 0$ with bond trees, bond animals and site animals. Similarly, the surface considered can be either penetrable or impenetrable, and, for each embedding, one can consider either counting the number of vertices in the surface or counting the number of edges in the surface. We will show that results analogous to (2.3)-(2.9) for walks can also be established for these models with κ and κ' being replaced by the corresponding growth connective constants. In the following, we will concentrate on the problem of n-vertex bond trees with number of vertices in the surface. The same arguments can also apply to the other cases with some possible minor modifications which will be pointed out later.

The partition functions for lattice bond trees rooted on the surface $x_1 = 0$ are defined as

$$T_n(\omega) = \sum_{i=1}^{n} t_{n,i} e^{i\omega}, \tag{4.12}$$

$$T_n^+(\omega) = \sum_{i=1}^{n} t_{n,i}^+ e^{i\omega}, \tag{4.13}$$

where $t_{n,i}$ denotes the number of distinct n-vertex trees which are rooted at the origin **0** and have i vertices in the surface, $t^+_{n,m}$ is the number of such trees that must lie on one side of the surface. For the other models, the corresponding partition functions are defined in the same fashion. Obviously, the partition functions (4.12) and (4.13) are non-decreasing functions of either n or ω with the other one being fixed. This property will be used quite often later without further mention. We prove the following results.

(1) The limits

$$\ln T(\omega) = \lim_{n\to\infty} \frac{1}{n} \ln T_n(\omega), \tag{4.14}$$

$$\ln T^+(\omega) = \lim_{n\to\infty} \frac{1}{n} \ln T^+_n(\omega) \tag{4.15}$$

exist for all ω.

(2) The limits $\ln T(\omega)$ and $\ln T^+(\omega)$ are continuous convex non-decreasing functions of ω satisfying

$$\max(\ln \lambda_0, \ln \lambda_0' + \omega) \le \ln T^+(\omega) \le \ln T(\omega) \le \max(\ln \lambda_0, \ln \lambda_0 + \omega), \tag{4.16}$$

where λ_0 and λ_0' are the growth constants of the d-dimensional and corresponding $(d-1)$-dimensional lattices respectively given by (1.13). These two inequalities then imply that there exist critical values ω_c and ω_c^+ defined by

$$\omega_c = \sup\{\omega : \ T(\omega) = \lambda_0\}, \qquad \omega_c^+ = \sup\{\omega : \ T^+(\omega) = \lambda_0\} \tag{4.17}$$

at which $T(\omega)$ and $T^+(\omega)$ are non-analytic.

4.2.1 The establishment of limits (4.14) and (4.15)

We establish the existence of the limit $T(\omega)$. The proof for $T^+(\omega)$ is the same.

Let $\mathcal{T}_{n_1}$ and $\mathcal{T}_{n_2}$ be sets of bond trees with n_1 and n_2 vertices respectively. Then

$$\mathcal{T}_{n_1} = \mathcal{T}_{n_1,1} \bigcup \cdots \bigcup \mathcal{T}_{n_1,n_1} \tag{4.18}$$

for $i = 1$ and $i = 2$, where $\mathcal{T}_{n_i,m}$ is the subset of $\mathcal{T}_{n_i}$ with m vertices on the surface $x_1 = 0$. We denote by $t_{n_i,m}$ the number of trees in $\mathcal{T}_{n_i,m}$. For every $\mathbf{T}_1 \in \mathcal{T}_{n_1,m_1}$ and $\mathbf{T}_2 \in \mathcal{T}_{n_2,m_2}$, we denote by $\mathcal{V}_1$ be the vertex set of $\mathbf{T}_1$ and $\mathcal{V}_2$ the vertex set of $\mathbf{T}_2$. Therefore, $\mathcal{V}_1$ and $\mathcal{V}_2$ are finite and their intersect is nonempty, since

$$\mathbf{0} \in \mathcal{V}_1 \bigcap \mathcal{V}_2. \tag{4.19}$$

We body shift $\mathbf{T}_2$ in the direction of x_d, which then does not change the configuration, therefore, the number of vertices of $\mathbf{T}_2$ in the surface. By a finite number of steps, we obtain that $d(\mathcal{V}_1, \mathcal{V}_2) = 1$. Then from theorem 4.1, there exists a vertex $\mathbf{v}_1 \in \mathcal{V}_1$ and a vertex $\mathbf{v}_2 \in \mathcal{V}_2$ such that

$$d(\mathbf{v}_1, \mathbf{v}_2) = 1 \tag{4.20}$$

with $\mathbf{v}_1 = (x_1, x_2, \ldots, x_d)$ and $\mathbf{v}_2 = (x_1, x_2, \ldots, x_d + 1)$. By adding an edge to join these two vertices, we obtain a $(n_1 + n_2)$-vertex tree $\mathbf{T}_3$ which has $m_1 + m_2$ vertices in the surface. We formally write

$$\mathbf{T}_3 = (\mathbf{T}_1, \mathbf{T}_2) \tag{4.21}$$

to indicate that $\mathbf{T}_3$ is obtained by body shifting $\mathbf{T}_2$ and connecting it to $\mathbf{T}_1$ as described above. Any distinct pair of $\mathbf{T}_1$ and $\mathbf{T}_2$ gives a distinct $\mathbf{T}_3$. We denote by $\mathcal{T}'_{n_1+n_2}$ the set of all such trees given by (4.21). $\mathcal{T}'_{n_1+n_2}$ can be considered as a direct product of $\mathcal{T}_{n_1}$ and $\mathcal{T}_{n_2}$ such that

$$\mathcal{T}'_{n_1+n_2} = \mathcal{T}_{n_1} \bigoplus \mathcal{T}_{n_2} = \{(\mathbf{T}_1, \mathbf{T}_2),\ \mathbf{T}_1 \in \mathcal{T}_{n_1} \text{ and } \mathbf{T}_2 \in \mathcal{T}_{n_2}\}.$$

Obviously, for the subset $\mathcal{T}_{n_1+n_2,m}$ of $\mathcal{T}_{n_1+n_2}$, we have

$$\mathcal{T}'_{n_1+n_2,m} = \left(\mathcal{T}_{n_1,1} \bigoplus \mathcal{T}_{n_2,m}\right) \bigcup \cdots \bigcup \left(\mathcal{T}_{n_1,m} \bigoplus \mathcal{T}_{n_2,1}\right) \tag{4.22}$$

with

$$\left(\mathcal{T}_{n_1,i} \bigoplus \mathcal{T}_{n_2,m-i}\right) \bigcap \left(\mathcal{T}_{n_1,j} \bigoplus \mathcal{T}_{n_2,m-j}\right) = \emptyset \tag{4.23}$$

for $i \neq j$. Since

$$\mathcal{T}'_{n_1+n_2,m} \subseteq \mathcal{T}_{n_1+n_2,m}, \tag{4.24}$$

we obtain

$$t_{n_1,1}t_{n_2,m} + \cdots + t_{n_1,m}t_{n_2,1} \leq t_{n_1+n_2,m+1}. \tag{4.25}$$

Multiplying both sides of equation (4.25) by $e^{(m+1)\omega}$ and summing over m gives

$$T_{n_1}(\omega)T_{n_2}(\omega) \leq T_{n_1+n_2}(\omega). \tag{4.26}$$

From (1.13) and (4.12), we obtain

$$\begin{aligned} \frac{1}{n}\ln T_n(\omega) &\leq \frac{1}{n}\ln\sum_{m=1} t_{n,m} + \omega \\ &\leq \frac{1}{n}\ln nt_n + \omega \leq \ln\lambda_0 + 1 + \omega \end{aligned} \tag{4.27}$$

where t_n is the number of trees in the bulk which is related to the number of rooted trees by a factor n, and we also use the that fact $n^{-1}\ln n < 1$ for any n. Then by theorem 4.3, we establish

$$\lim_{n\to\infty}\frac{1}{n}\ln T_n(\omega) = \sup_{n>0}\frac{1}{n}\ln T_n(\omega) \equiv \ln T(\omega). \tag{4.28}$$

4.2.2 The existence of a critical point

Since $T_n(\omega)$ is a non-decreasing function of ω, and for fixed n, T_n is a polynomial in e^ω and therefore, bounded in any fixed closed interval of ω. Consequently (Hardy *et al* [63]), to establish that $\ln T_n(\omega)$ is a convex function of ω, it is enough to show that

$$\frac{1}{2}\ln T_n(\omega_1) + \frac{1}{2}\ln T_n(\omega_2) \geq \ln T_n(\frac{1}{2}\omega_1 + \frac{1}{2}\omega_2) \tag{4.29}$$

for any ω_1, ω_2. By Cauchy's inequality

$$\begin{aligned} T_n(\omega_1)T_n(\omega_2) &= \sum_{m=1}^{n} t_{n,m}e^{m\omega_1}\sum_{m=1}^{n} t_{n,m}e^{m\omega_2} \\ &\geq \left(\sum_{m=1}^{n} t_{n,m}e^{m(\omega_1+\omega_2)/2}\right)^2 = (T_n((\omega_1+\omega_2)/2))^2, \end{aligned} \tag{4.30}$$

which proves (4.29). Now, if the limit of a sequence of convex functions exists, that limit is also a convex function. Hence $\ln T(\omega)$, and similarly $\ln T^+(\omega)$ defined by (4.14) and (4.15) are both non-decreasing convex functions of ω for all real ω.

To derive (4.16), we let t_n^+ be the number of trees with n vertices satisfying $x_1 \geq 0$, and $t_{n,1}^+$ the number of such trees with only its root in the surface $x_1 = 0$. Then, for $\omega \leq 0$, we have

$$t_{n-1}^+ e^{\omega} = t_{n,1}^+ e^{\omega} \leq T_n^+(\omega) \leq T_n(\omega) \leq T_n(0) \leq n t_n, \tag{4.31}$$

where t_n is given in (1.13). Since

$$\lim_{n\to\infty} \frac{1}{n} \ln t_{n-1}^+ = \lim_{n\to\infty} \frac{1}{n} \ln t_n^+ = \lim_{n\to\infty} \frac{1}{n} \ln t_n = \ln \lambda_0 \tag{4.32}$$

(Whittington and Soteros [17]), we obtain for $\omega \leq 0$,

$$\ln \lambda_0 \leq \ln T^+(\omega) \leq \ln T(\omega) \leq \ln \lambda_0. \tag{4.33}$$

For $\omega \geq 0$, we have

$$t_{n,n}^+ e^{n\omega} \leq T_n^+(\omega) \leq T_n(\omega) \leq n t_n e^{n\omega}. \tag{4.34}$$

Since $t_{n,n}^+ = n t_n'$, where t' is the total number of trees wholly embedded in the $(d-1)$-dimensional surface $x_1 = 0$,

$$\lim_{n\to\infty} \frac{1}{n} \ln t_{n,n}^+ = \lim_{n\to\infty} \frac{1}{n} \ln n t_n' = \ln \lambda_0', \tag{4.35}$$

λ_0' is the growth constant of trees in $(d-1)$-dimensional lattice. This gives

$$\ln \lambda_0 + \omega \leq \ln T^+(\omega) \leq \ln T(\omega) \leq \ln \lambda_0 + \omega. \tag{4.36}$$

The inequalities (4.33) and (4.36) give (4.16) and imply that there exist critical points (transition points) ω_c and ω_c^+ given by

$$\omega_c = \sup\{\omega : \ T(\omega) = \lambda_0'\}, \quad \omega_c^+ = \sup\{\omega : \ T^+(\omega) = \lambda_0'\}. \tag{4.37}$$

at which $T(\omega)$ and $T^+(\omega)$ are respectively non-analytic. By analogy, two crossover exponents ϕ and ϕ^+ can also be defined at the transition points by

$$\ln T(\omega) - \ln T(\omega_c) \sim (\omega - \omega_c)^{1/\phi}, \quad \omega > \omega_c, \tag{4.38}$$

$$\ln T^+(\omega) - \ln T^+(\omega_c) \sim (\omega - \omega_c^+)^{1/\phi^+}, \quad \omega > \omega_c^+. \tag{4.39}$$

The numerical estimates of the transition points are given in section 4.6.

4.2.3 Other cases

By following exactly the same arguments, we can establish the existence of the limits (4.14) and (4.15) for bond animals and site animals by counting the number of their vertices in the surface. For the problems of bond trees and bond animals in which one is interested in the number of edges in the surface, a difference arises when establishing the inequality (4.26). For instance, for bond trees, adding an edge to join $\mathbf{T}_1$ and $\mathbf{T}_2$ results in a new tree $\mathbf{T}_3$ containing $n_1 + n_2 + 1$ edges with either $m_1 + m_2$ or $m_1 + m_2 + 1$ of them in the surface. If we still denote by $T'_n(\omega)$ the partition function for such trees, equation (4.26) is replaced by

$$T'_{n_1}(\omega)T'_{n_2}(\omega) \leq (1 + e^{-\omega})T'_{n_1+n_2+1}(\omega). \tag{4.40}$$

The existence of the limit analogous to (4.14) is established by using corollary 4.1. For the model of site animals with edges in the surface, one more step body shift is needed, i.e. we require that $d(\mathcal{V}_1, \mathcal{V}_2) = 2$. Then there exist $\mathbf{v}_1 = (x_1, x_2, \ldots, x_d) \in \mathcal{V}_1$ and $\mathbf{v}_2 = (x_1, x_2, \ldots, x_d + 2) \in \mathcal{V}_2$. We add the vertex $\mathbf{v}_1 + \mathbf{e}_d$, which may have some vertices of $\mathcal{V}_1$ and $\mathcal{V}_2$ other than $\mathbf{v}_1$ and $\mathbf{v}_2$ in its nearest neighbourhood. From the definition of site animals, we need to add all corresponding edges to connect $\mathbf{v}_1 + \mathbf{e}_d$ with these vertices, which results in a new site animal having at most $2d$ extra edges and at most $2(d-1)$ extra edges in the surface. The inequality analogous to (4.40) is then given as

$$A'_{n_1}(\omega)A'_{n_2}(\omega) \leq 2d(1 + e^{-\omega} + \cdots + e^{-2(d-1)\omega})A'_{n_1+n_2+2d}(\omega), \tag{4.41}$$

where we denote by $A'_n(\omega)$ the partition function for site animals with number of edges in the surface. By using corollary 4.1 again, we establish (4.14).

From the same arguments for n-vertex trees, we can show that the reduced free energy of all these models are non-decreasing convex functions of ω and bounded by the inequalities analogous to (4.16) with λ_0 and λ'_0 being replaced by the corresponding growth constants.

Even though, by analogy, one would expect the same results for site trees, we are unable to show the existence of the limits (4.14) and (4.15) for site trees embedded in a general d-dimensional hypercubic lattice. However, with the assumption of the existence of (4.14) and (4.15), one can obtain (4.16) for site trees by using the same arguments for bond trees. The previous arguments for site animals with number of edges in the surface have indicated that a directed concatenation of two site trees may not result in a site tree. In section 4.5, we will discuss a special case: site trees embedded in the square lattice, where, by following a modified approach, we will show the existence of the reduced free energy (4.14) and (4.15) for site trees in the square lattice.

4.3 Lattice bond trees with restricted number of branch points

In this section, we examine the interaction between the adsorption surface and bond trees with a restriction on the number of the branch points. We derive some properties for the reduced free energy which will be used in the next section. In the remainder of this chapter, we will not distinguish the surface each time. However, it is understood that the corresponding results should apply.

We denote by $\mathcal{T}_n(\epsilon, \leq)$ the set of n-vertex trees which contain at most ϵn vertices of degree greater than 2. $\mathcal{T}_{n,i}(\epsilon, \leq)$ is a subset of $\mathcal{T}_n(\epsilon, \leq)$, which contains all n-vertex trees with i vertices in the surface and $t_{n,i}(\epsilon, >)$ is the number of trees in $\mathcal{T}_{n,i}(\epsilon, \leq)$.

Theorem 4.4 *There exists* $T(\epsilon,\omega) > 0$ *such that*

$$\lim_{n\to\infty} \frac{1}{n} \ln T_n(\epsilon, \leq, \omega) = \lim_{n\to\infty} \frac{1}{n} \ln \sum_{i=1}^{n} t_{n,i}(\epsilon, \leq, \omega) e^{i\omega} = \ln T(\epsilon,\omega), \tag{4.42}$$

and $\ln T(\epsilon,\omega)$ *is a concave function of* ϵ *in* $[0, 1]$.

Proof: Consider two trees $\mathbf{T}_1 \in \mathcal{T}_{n_1,i_1}(\epsilon_1, \leq)$ with a vertex set $\mathcal{V}_1$ and $\mathbf{T}_2 \in \mathcal{T}_{n_2,i_2}(\epsilon_2, \leq)$ with a vertex set $\mathcal{V}_2$. We body shift $\mathbf{T}_2$ in the direction of x_d by a finite number of steps such that $d(\mathcal{V}_1, \mathcal{V}_2) = q + 1$, where q is some positive integer. Then there exists a vertex $\mathbf{v}_1 \in \mathcal{V}(t_1)$ and a vertex $\mathbf{v}_2 \in \mathcal{V}_2$ such that $\mathbf{v}_1 = (x_1^1, x_2^1, \ldots, x_d^1)$ and $\mathbf{v}_2 = (x_1^2, x_2^2, \ldots, x_d^2 + q + 1)$. By adding a q-step SAW $\{\mathbf{v}_1, \mathbf{v}_1 + \mathbf{e}_d, \ldots, \mathbf{v}_1 + q\mathbf{e}_d, \mathbf{v}_2\}$, we obtain a new tree $\mathbf{T}_3$ with $n_1 + n_2 + q$ vertices and either $i_1 + i_2$ or $i_1 + i_2 + q$ of them in the surface. $\mathbf{T}_3$ can have at most $\epsilon_1 n_1 + \epsilon_2 n_2 + 2$ vertiecs of degree greater than 2. Therefore, choosing q to be the smallest integer greater or equal to $2/\epsilon'$ ensures that $\mathbf{T}_3 \in \mathcal{T}_{n_1+n_2+q,i_1+i_2}(\epsilon', \leq)$ or $\mathcal{T}_{n_1+n_2+q,i_1+i_2+q}(\epsilon', \leq)$, where $\epsilon' = (\epsilon_1 n_1 + \epsilon_2 n_2)/(n_1 + n_2)$. This construction produces a unique $\mathbf{T}_3$ for each pair $\mathbf{T}_1$ and $\mathbf{T}_2$ but not all members of $\mathcal{T}_{n_1+n_2+q}(\epsilon', \leq)$ can be obtained in this fashion. Following the arguments in section 4.2.1, we obtain

$$t_{n_1,i_1}(\epsilon_1, \leq) t_{n_2,i_2}(\epsilon_2, \leq) \leq t_{n_1+n_2+q,i_1+i_2}(\epsilon', \leq) + t_{n_1+n_2+q,i_1+i_2+q}(\epsilon', \leq). \tag{4.43}$$

Multiplying both sides with $e^{(i_1+i_2)\omega}$ and summing over $i_1 + i_2$ yields

$$T_{n_1}(\epsilon_1, \leq, \omega) T_{n_2}(\epsilon_2, \leq, \omega) \leq (1 + e^{q|\omega|}) T_{n_1+n_2+q}(\epsilon', \leq, \omega). \tag{4.44}$$

Putting $\epsilon_1 = \epsilon_2 = \epsilon$ in (4 44) gives

$$T_{n_1}(\epsilon, \leq, \omega) T_{n_2}(\epsilon, \leq, \omega) \leq (1 + e^{|\omega|}) T_{n_1+n_2+q}(\epsilon, \leq, \omega) \tag{4.45}$$

Since $\mathcal{T}_{n,i}(\epsilon, \leq) \subseteq \mathcal{T}_{n,i}$, $T_n(\epsilon, \leq, \omega) \leq T_n(\omega)$. From (4.27), $n^{-1} \ln T_n(\epsilon, \leq, \omega)$ is bounded above for any ω. From theorem 4.3, there exists $T(\epsilon,\omega) > 0$ such that

$$\lim_{n\to\infty} \frac{1}{n} \ln T_n(\epsilon, \leq, \omega) = \ln T(\epsilon,\omega) < \infty. \tag{4.46}$$

Now put $n_1 = n_2 = n$ in equation (4.44). This gives

$$T_n(\varepsilon_1, \leq, \omega) T_n(\varepsilon_2, \leq, \omega) \leq (1 + e^{q|\omega|}) T_{2n+q}((\varepsilon_1 + \varepsilon_2)/2, \leq, \omega). \tag{4.47}$$

Taking logarithm, dividing by n and taking the limit $n \to \infty$ with ε_1 and ε_2 fixed, we have

$$\ln T(\varepsilon_1, \omega) + \ln T(\varepsilon_2, \omega) \leq 2 \ln T((\varepsilon_1 + \varepsilon_2)/2, \omega). \tag{4.48}$$

Since $\ln T(\varepsilon, \omega)$ is a bounded non-decreasing function of ε, equation (4.48) implies that $\ln T(\varepsilon, \omega)$ is a concave function of ε for $\varepsilon \in [0, 1]$(Hardy *et al* [63]).

For the function $\ln T(\varepsilon, \omega)$, one can have the following propositions:

Proposition 4.1 *For any* ω, $\ln T(0, \omega) < \ln T(1, \omega)$.

Proof: It is clear that $\mathcal{T}_{n,i}(0, \leq) = \mathcal{S}_{n,i}(2)$, the set of all nonuniform 2-star of n vertices with i of them in the surface and $\mathcal{T}_{n,i}(1, \leq) = \mathcal{T}_{n,i}$, the set of trees of n vertices of which i of them are in the surface. Therefore, we have

$$\ln T(0, \omega) = A(\omega), \tag{4.49}$$

and

$$\ln T(1, \omega) = \ln T(\omega), \tag{4.50}$$

where $A(\omega)$ and $\ln T(\omega)$ are given by (2.3) and (4.14) respectively.

For $\omega \leq 0$, from (2.5) and (4.16), $A(\omega) \equiv \kappa$ and $\ln T(\omega) \equiv \ln \lambda_0$. Since $\kappa < \ln \lambda_0$ (Gaunt *et al* [20]), we obtain that, for $\omega \leq 0$,

$$\ln T(0, \omega) < \ln T(1, \omega). \tag{4.51}$$

For $\omega \geq 0$, from (2.44) and (4.26),

$$A(\omega) \leq \frac{1}{n} \ln S_n(2, \omega), \tag{4.52}$$

$$\ln T(\omega) \geq \frac{1}{n} \ln T_n(\omega). \tag{4.53}$$

Since for any n,

$$S_n(2,\omega) < T_n(\omega). \tag{4.54}$$

We have, for $\omega \geq 0$,

$$A(\omega) < \ln T(\omega), \tag{4.55}$$

or

$$\ln T(0,\omega) < \ln T(1,\omega). \tag{4.56}$$

Therefore, for any ω,

$$\ln T(0,\omega) < \ln T(1,\omega). \tag{4.57}$$

Proposition 4.2 *For any ω, $\ln T(\varepsilon,\omega)$ is a continuous function of ε in $[0, 1)$.*

Proof: Since $\ln T(\varepsilon,\omega)$ is a non-decreasing concave function of $\varepsilon \in [0, 1]$, it is continuous for $\varepsilon \in (0, 1)$ (Hardy *et al* [63]). One only need establish the continuity at $\varepsilon = 0$. Let n_k be the number of vertices of degree k in a tree. Let $u_{n,i}(\varepsilon)$ be the number of n-vertex trees with i vertices in the surface and containing at most εn vertices of degree not equal to 2. Then we have

$$t_{n,i}(\varepsilon,\leq) \leq u_{n,i}(2d\varepsilon), \tag{4.58}$$

since, from Euler's formula (3.1),

$$m = n_1 + \sum_{i\geq 3} n_i = 2 + \sum_{i\geq 3}(i-1)n_i \leq 2d\varepsilon n \tag{4.59}$$

provided that $\frac{2}{n} \leq \varepsilon \leq \frac{1}{2d}$. Therefore, we have

$$T_n(\varepsilon,\leq,\omega) = \sum_{i=1}^{n} t_{n,i}(\varepsilon,\leq)e^{i\omega} \leq \sum_{i=1}^{n} u_{n,i}(2d\varepsilon)e^{i\omega} = U_n(2d\varepsilon,\omega). \tag{4.60}$$

By following arguments in section 3.3.5, we can bound $U(2d\varepsilon,\omega)$ by

$$U_n(2d\varepsilon,\omega) \leq \sum_{m\leq 2d\varepsilon n} T(m)\begin{pmatrix} n-2 \\ m-2 \end{pmatrix}(n-2)e^{nA(\omega)+o(n)}, \tag{4.61}$$

where $T(m)$ is the number of ways to connect all m vertices of degree not equal to 2. Since there exist positive constants B and β (Otter [64]) such that

$$T(m) \leq B\beta^m, \tag{4.62}$$

we obtain

$$T_n(\epsilon,\omega) \leq U_n(2d\epsilon,\omega) \leq (2d)\epsilon n B\beta^{(2d\epsilon n)} \begin{pmatrix} n-2 \\ 2d\epsilon n-2 \end{pmatrix} e^{nA(\omega)+o(n)} \tag{4.63}$$

provided that $\epsilon \leq \frac{1}{2dn} + \frac{1}{4d}$. It has been shown by Madras *et al* [65] that for any $a > 0$ and $b > 0$,

$$\lim_{n\to\infty} \frac{1}{n} \ln \begin{pmatrix} an \\ bn \end{pmatrix} = a\ln a - b\ln b - (a-b)\ln(a-b). \tag{4.64}$$

Therefore, in (4.63), taking logarithm, dividing by n and taking the limit $n \to \infty$, we have

$$\begin{aligned} \ln T(\epsilon,\omega) &= \lim_{n\to\infty} \frac{1}{n} \ln T(\epsilon, \leq, \omega) \qquad (4.65) \\ &\leq (2d\epsilon)\ln\beta - (2d\epsilon)\ln(2d\epsilon) - (1-2d\epsilon)\ln(1-2d\epsilon) + A(\omega). \end{aligned}$$

Letting $\epsilon \to 0$ in (4.65) yields

$$\lim_{\epsilon\to 0} \ln T(\epsilon,\omega) = A(\omega) = \ln T(0,\omega), \tag{4.66}$$

which establishes the continuity of $\ln T(\epsilon,\omega)$ at $\epsilon = 0$.

4.4 Weakly embedded animals with cyclomatic index c

In the bulk, n-vertex bond trees and n-vertex bond animals with cyclomatic index c are related by equations (1.18) and (1.20). In this section, it will be shown that these relations also hold in the presence of a surface interaction. Precisely, we will show that

$$\lim_{n\to\infty} \frac{1}{n} \ln A_n(c,\omega) = \lim_{n\to\infty} \frac{1}{n} \ln \sum_{i=1}^{n} a_{n,i}(c) e^{i\omega} = \ln T(\omega), \tag{4.67}$$

where $a_{n,i}(c)$ denotes the number of c-animals with n vertices of which i of them are in the surface, and $\ln T(\omega)$ is given by (4.14). If we assume that, as $n \to \infty$,

$$A_n(c,\omega) \sim (T(\omega))^n n^{-\theta_c(\omega)}, \tag{4.68}$$

then,

$$\theta_c(\omega) = \theta_0(\omega) - c \tag{4.69}$$

for all ω. This result can also be generalized to the case where there is a monomer-monomer interaction that competes with the monomer-surface interaction (Zhao and Lookman [66]).

4.4.1 An upper bound on $A_n(c,\omega)$

It has been shown by Whittington *et al* [21] that, by deleting the top edge of one cycle (the top edge in the edge set consisting of all edges in the cycle) of a c-animal, one converts the c-animal into a $(c-1)$-animal of n vertices. The resulting $(c-1)$-animal can have at most $(2dn)$ c-animals as its precursors. Since this procedure does not change the positions of all n vertices in the lattice, the resulting $(c-1)$-animal has the same number of vertices in the surface as the c-animal does. Therefore, one has

$$a_{n,i}(c) \leq (2dn)a_{n,i}(c-1). \tag{4.70}$$

Repeating the same procedure c times gives

$$a_{n,i}(c) \leq (2dn)^c a_{n,i}(0) = (2dn)^c t_{n,i}. \tag{4.71}$$

Multiplying both sides with $e^{i\omega}$ and summing over i yields

$$A_n(c,\omega) \leq (2dn)^c T_n(\omega). \tag{4.72}$$

4.4.2 A lower bound on $A_n(c,\omega)$

Such a lower bound is obtained by generalizing the arguments of Soteros and Whittington [22] taking into account the existence of the surface.

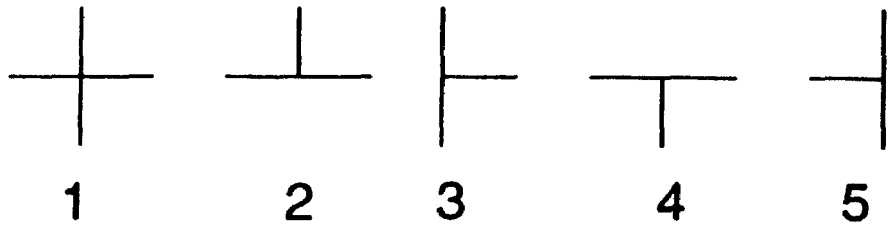


Figure 4.1: On the square lattice, a vertex of degree greater than two must be one of the five types shown

For convenience, we concentrate on c-animals embedded in the square lattice. However, the results can be generalized to the d-dimensional hypercubic lattice. In the square lattice, a vertex has coordinates (x, y). The adsorption "surface" is $x = 0$. A vertex is a member of $\mathcal{V}_1$ if it is of degree 4 and is a member of $\mathcal{V}_2$, $\mathcal{V}_3$, $\mathcal{V}_4$ or $\mathcal{V}_5$ if it is of degree 3 and is not connected to the neighbouring vertex in south, west, north or east direction respectively (Figure 4.1). Let $\mathcal{V}'$ be one of them.

Theorem 4.5 *Every n-vertex tree containing a vertex $\mathbf{v}_0 \in \mathcal{V}'$ can be converted into a 1-animal (with $n+1$ vertices) containing a 4-cycle in which $\mathbf{v}_0$ is the bottom (or top) vertex of the 4-cycle. The resulting 1-animal can have at most three trees rooted at a vertex in $\mathcal{V}'$ as precursors.*

Proof: Let $\mathbf{v}_t$ be the top vertex of the tree with coordinates (x_t, y_t). Without loss of the generality, we let $\mathbf{v}_0 \in \mathcal{V}' = \mathcal{V}_1$, then v_0 is connected to $\mathbf{v}_1$ and $\mathbf{v}_2$ with coordinates $(x+1, y)$ and $(x, y+1)$ respectively. We consider three subcases as follows.

(i) There is no vertex in the tree with coordinates $(x+1, y+1)$ (in this case $\mathbf{v}_0 \in \mathcal{W}_1$).

(ii) There is a vertex $\mathbf{v}_3 \in \mathcal{V}$ with coordinates $(x+1, y+1)$ and either $[\mathbf{v}_1, \mathbf{v}_3] \in \mathcal{E}$ or $[\mathbf{v}_2, \mathbf{v}_3] \in \mathcal{E}$ (then $\mathbf{v}_0 \in \mathcal{W}_2$).

(iii) $v_3 \in \mathcal{V}$ but both of the edges $[v_1, v_3]$, $[v_2, v_3]$ are not in the set $\mathcal{E}$ (then $v_0 \in \mathcal{W}_3$).

For the three cases, we have three different constructions.

(i) Add v_3 at $(x+1, y+1)$ and the edges $[v_1, v_3]$ and $[v_2, v_3]$.

(ii) If $[v_1, v_3] \in \mathcal{E}$, add $[v_2, v_3]$, and the vertex $v_{t'}$ with coordinates $(x_t + 1, y_t)$ and the edge $[v_t, v_{t'}]$. If $[v_2, v_3] \in \mathcal{E}$, add $[v_1, v_3]$ and the vertex $v_{t''}$ with coordinates $(x_t, y_t + 1)$ and the edge $[v_t, v_{t''}]$.

(iii) The tree must contain at least one of two vertices with coordinates $(x+2, y+1)$ and $(x+1, y+2)$. We call these vertices v_4 and v_5 respectively. In addition, at least one of the edges $e_4 = [v_3, v_4]$ and $e_5 = [v_3, v_5]$ must be a member of $\mathcal{E}$. v_3 is connected to v_0 through one and only one of e_4 and e_5. Delete the edge e_4 or e_5 on this connected path, add the edges $[v_1, v_3]$ and $[v_2, v_3]$ and the vertex $v_{t'} = (x_t + 1, y_t)$ and the edge $[v_t, v_{t'}]$ if e_4 is deleted, or the vertex $v_{t''} = (x_t, y_t + 1)$ and the edge $[v_t, v_{t''}]$ if e_5 is deleted.

The connected graph resulting from each of these constructions has $n+1$ vertices and $n+1$ edges so that it is a 1-animal. Under the transformation, any two trees which differ only by having the vertex v_0 in different $\mathcal{W}_i$ may result in the same 1-animal. Since $i = 3$, the 1-animal can have at most three trees as its precursors.

For v_0 in the other four sets, we follow the same procedure except that we will examine the vertex v_3' with coordinates $(x-1, y-1)$ for $v_0 \in \mathcal{V}_4$ or $\mathcal{V}_5$.

Within the procedure, the number of vertices of the tree in the surface is unchanged. Therefore, if the tree has i vertices in the surface, the resulting 1-animal can have either i or $i+1$ vertices in the surface.

We denote by $b_{n,i}(\varepsilon)$ the number of n-vertex trees with i vertices in the surface and containing more than εn vertices which are members of $\mathcal{V}'$, one of $\mathcal{V}_1$, $\mathcal{V}_2$, $\mathcal{V}_3$, $\mathcal{V}_4$

and $\mathcal{V}_5$. Then, from theorem 4.5, we have

$$a_{n+1,i}(1) + a_{n+1,i+1}(1) \geq \binom{\epsilon n}{1} b_{n,i}(\epsilon)/3 \tag{4.73}$$

for any ϵ such that $\epsilon n \geq 1$, since there are at least

$$\binom{\epsilon n}{1} \tag{4.74}$$

ways to choose v_0. Similarly, if $\epsilon n \geq c$, we can have

$$\binom{\epsilon n}{c} \tag{4.75}$$

ways to choose c vertices. By carrying out the above transformation at these c vertices successively, we obtain a c-animal which has $n + c$ vertices with $i + j$ of them in the surface where $0 \leq j \leq c$. Hence, we have

$$a_{n+c,i}(c) + a_{n+c,i+1}(c) + \cdots + a_{n+c,i+c}(c) \geq \binom{\epsilon n}{c} b_{n,i}(\epsilon)/3^c \tag{4.76}$$

for $\epsilon n \geq c$.

Now, we derive a lower bound on $b_{n,i}(\epsilon)$.

Lemma 4.1 *Let $\mathcal{T}_{n,i}(\epsilon, >)$ be the set of n-vertex trees with i vertices in the surface containing more than ϵn vertices of degree greater than 2 and $t_{n,i}(\epsilon, >)$ be the number of trees in $\mathcal{T}_{n,i}(\epsilon, >)$, then*

$$b_{n,i}(\epsilon/5) \geq t_{n,i}(\epsilon, n)/5. \tag{4.77}$$

Proof: Let $\mathcal{T}_{n,i}(\epsilon, >)$ be the set of n-vertex trees with i vertices in the surface and containing more than ϵn vertices of degree greater than 2. We construct subsets $\mathcal{T}^m_{n,i}(\epsilon, >)$ such that a tree $\mathbf{T} \in \mathcal{T}_{n,i}$ is a member of $\mathcal{T}^m_{n,i}(\epsilon, >)$ if m is the smallest number such that the number of vertices in $\mathcal{V}_m(\mathbf{T})$ is at least as large as the number in $\mathcal{V}_k(\mathbf{T})$, $k = 1, \ldots, 5$, $k \neq m$. Thus, $\mathbf{T}$ can be a member of only one subset $\mathcal{T}^m_{n,i}(\epsilon, >)$. Let $\mathcal{V}'$ be $\mathcal{V}_m$ such that

$$|\mathcal{T}^m_{n,i}(\epsilon, >)| = \max\{|\mathcal{T}^j_{n,i}(\epsilon, >)|, \quad j = 1, \ldots, 5\} \tag{4.78}$$

where $|\cdot|$ denotes the cardinality of a set. From the definitions of $\mathcal{T}_{n,i}(\varepsilon,>)$ and $\mathcal{T}^j_{n,i}(\varepsilon,>)$, there must be at least $\varepsilon n/5$ vertices in $V' = V_m$. We obtain

$$b_{n,i}(\varepsilon/5) \geq |\, T^m_{n,i}(\varepsilon,>)\,| \geq \sum_{j=1}^{5} |\, \mathcal{T}^j_{n,i}(\varepsilon,>)\,|/5 \geq |\, \mathcal{T}_{n,i}(\varepsilon,>)\,|/5 = t_{n,i}(\varepsilon,>)/5. \quad (4.79)$$

From (4.76) and (4.77), we have

$$a_{n+c,i}(c) + \ldots + a_{n+c,i+c}(c) \geq \binom{\varepsilon' n}{c} t_{n,i}(\varepsilon)/5 \cdot 3^c \quad (4.80)$$

with $\varepsilon' = \varepsilon/5$. Multiplying both sides with $e^{i\omega}$ and summing over i gives

$$c \cdot (1 + e^{|\omega|} + \ldots + e^{c|\omega|}) A_{n+c}(c,\omega) \geq \binom{\varepsilon' n}{c} T_n(\varepsilon,>,\omega)/5 \cdot 3^c. \quad (4.81)$$

Lemma 4.2 *For any ω, there exists $\varepsilon_0(\omega) > 0$, a constant $C(\omega)$ and an integer $N(\omega)$ such that for any $\varepsilon \leq \varepsilon_0(\omega)$ and $n \geq N(\omega)$,*

$$A_{n+c}(c,\omega) \geq C(\omega) \binom{\varepsilon' n}{c} T_n(\omega) \quad (4.82)$$

with $\varepsilon' = \varepsilon/5$.

Proof: It is obvious that for any $\varepsilon > 0$,

$$\mathcal{T}_{n,i} = \mathcal{T}_{n,i}(\varepsilon,\leq) \bigcup \mathcal{T}_{n,i}(\varepsilon,>), \quad (4.83)$$

and

$$\mathcal{T}_{n,i}(\varepsilon,\leq) \bigcap \mathcal{T}_{n,i}(\varepsilon,>) = \emptyset, \quad (4.84)$$

where $\mathcal{T}_{n,i}(\varepsilon,\leq)$, defined in section 4.3, is the set of n-vertex trees with i vertices in the surface and containing at most εn vertices of degree greater than 2. Then, one has

$$t_{n,i} = t_{n,i}(\varepsilon,\leq) + t_{n,i}(\varepsilon,>), \quad (4.85)$$

and

$$T_n(\omega) = T_n(\varepsilon,\leq,\omega) + T_n(\varepsilon,>,\omega). \quad (4.86)$$

From (4.14) and (4.46), we can write

$$T_n(\varepsilon, \leq, \omega) = [T(\varepsilon, \omega)]^n \cdot e^{o(n)}, \tag{4.87}$$

and

$$T_n(\omega) = [T(\omega)]^n \cdot e^{o(n)}. \tag{4.88}$$

Substituting these two equations into (4.88), we obtain

$$\begin{aligned} \frac{T_n(\varepsilon, >, \omega)}{T_n(\omega)} &= 1 - \frac{T_n(\varepsilon, \leq, \omega)}{T_n(\omega)} \\ &= 1 - \left(\frac{T(\varepsilon, \omega)}{T(\omega)}\right)^n e^{o(n)}. \end{aligned} \tag{4.89}$$

From proposition 4.1 and 4.2, for any ω, $T(\varepsilon, \omega)$ is continuous for $\varepsilon \in [0, 1)$ and $T(0, \omega) < T(1, \omega) = T(\omega)$. Therefore, there exists $\varepsilon_0(\omega) > 0$ such that for any $\varepsilon \leq \varepsilon_0(\omega)$,

$$T(\varepsilon, \omega) < T(\omega). \tag{4.90}$$

Therefore, for this ε,

$$\lim_{n \to \infty} \left(1 - \left(\frac{T(\varepsilon, \omega)}{T(\omega)}\right)^n e^{o(n)}\right) = 1. \tag{4.91}$$

Hence, there exists an integer $N(\omega)$ and a positive constant $C_1(\omega)$ such that for all $n > N(\omega)$

$$\frac{T_n(\varepsilon, >, \omega)}{T_n(\omega)} = 1 - \left(\frac{T(\varepsilon, \omega)}{T(\omega)}\right)^n e^{o(n)} \geq C_1(\omega), \tag{4.92}$$

or

$$T_n(\varepsilon, >, \omega) \geq C_1(\omega) T_n(\omega). \tag{4.93}$$

From (4.81) and (4.93), we obtain

$$A_{n+c}(c, \omega) \geq C(\omega) \binom{\varepsilon' n}{c} T_n(\omega), \tag{4.94}$$

where $C(\omega) = C_1(\omega)[c \cdot (1 + e^{|\omega|} + \ldots + e^{c|\omega|})]^{-1}$ and $\varepsilon' \leq \varepsilon_0(\omega)/5$.

The same inequality also can be obtained for a d-dimensional hypercubic lattice. In such a lattice, we classify all branch points by their degrees and by the way they connect with their nearest neighbour vertices. There are a total

$$k = \sum_{i=3}^{2d} \binom{2d}{j} = 2^{2d} - 2d^2 - d - 1 \tag{4.95}$$

such sets. In each set, a cycle is introduced at a branch point in the same fashion. Then in lemma 4.1, the inequality corresponding to (4.77) is

$$b_{n,i}(\epsilon/k) \geq t_{n,i}(\epsilon, \leq)/k. \tag{4.96}$$

From (4.72) and (4.94), we obtain

Theorem 4.6 *For given ω,*

$$\lim_{n\to\infty} \frac{1}{n} \ln A_n(c,\omega) = \ln T(\omega) \tag{4.97}$$

and, if the limit

$$\lim_{n\to\infty} \frac{\ln A_n(0,\omega) - n \ln T(\omega)}{\ln n} = -\theta_0(\omega) \tag{4.98}$$

exists, then the limit

$$\lim_{n\to\infty} \frac{\ln A_n(c,\omega) - n \ln T(\omega)}{\ln n} = -\theta_c(\omega) \tag{4.99}$$

also exists for all c and

$$\theta_c(\omega) = \theta_0(\omega) - c. \tag{4.100}$$

4.4.3 n-edge c-animals

As is mentioned, for an embedding, the interaction can also considered by counting the number of its edges in the surface. There is an interesting question: Can we derive the analogous results of (4.97) and (4.100) between n-edge trees and n-edge c-animals with number of edges in the surface? In the bulk, such a problem is very trivial, since if we denote by t'_n, t_n, $a'_n(c)$ and $a_n(c)$ the number of trees and c-animals

with n edges and n vertices respectively, then from Euler's formula (3.1) and (3.2), we have $t'_n = t_{n+1}$ and $a'_{n+c}(c) = a_n(c)$. But it is not a trivial problem with the presence of an adsorption surface, since the partition functions for these embeddings no longer have such clear relations. However, we can show that for such a problem, the analogous results can also exist.

We denote by $a'_{n,i}(c)$ the number of n-edge c-animals with i edges in the surface ($a'_{n,i}(0) = t'_{n,i}$). From the arguments given in section 4.4.1, we immediately obtain

$$a'_{n,i}(c) \leq (2dn)[a'_{n-1,i-1}(c-1) + a'_{n-1,i}(c-1)], \tag{4.101}$$

or

$$a_{n,i}(c)' \leq (2d)^c n(n-1)\cdots(n-c+1)[t_{n,i-c}' + \cdots + t'_{n,i}]. \tag{4.102}$$

Multiplying both sides with $e^{i\omega}$ and summing over i yields

$$A'_n(c,\omega) \leq (2d)^c n(n-1)\cdots(n-c+1) f(\omega) T'_n(\omega). \tag{4.103}$$

where $f(\omega) = c(1 + e^{|\omega|} + \cdots + e^{c|\omega|})$.

But an inequality analogous to (4.94) cannot be obtained by the arguments in section 3.5.2. From the previous procedure, one can see that such an inequality is deduced by proposition 4.1 and 4.2. We are unable to prove proposition 4.1 for the edge counting problem. However, by using a different approach to be introduced in the next section, we can derive the inequality analogous to (4.94). Combining these two inequalities will yield

Theorem 4.7 *For given ω,*

$$\lim_{n\to\infty} \frac{1}{n} \ln A'_n(c,\omega) = \ln T'(\omega), \tag{4.104}$$

and, if we assume that

$$A'_n(c,\omega) \sim n^{-\theta'_c(\omega)}[T'_n(\omega)]^n, \tag{4.105}$$

then

$$\theta'_c(\omega) = \theta'_0(\omega) - c \tag{4.106}$$

if either of them exists.

4.5 Strong embeddings in the square lattice

In section 4.2 we have shown that in a general d-dimensional lattice, an adsorption transition exists for lattice animals and lattice bond trees. We have also mentioned that the same result can also be established for site trees embedded in the square lattice. In this section, instead of only establishing the limit (4.14) for site trees, we consider the interaction between site c-animals and an adsorption surface. We show that theorem 4.6 also holds for site c-animals in the square lattice. In other words, if we denote by $a^s_{n,i}(c)$ the number site c-animals ($a^s_{n,i}(0) = t^s_{n,i}$, the number of site trees) with n vertices of which i of them are in the "surface" $x = 0$, we show that the limit

$$\lim_{n\to\infty} \frac{1}{n} \ln \sum_{i=1}^{n} a^s_{n,i}(c) e^{i\omega} = \lim_{n\to\infty} \frac{1}{n} \ln \sum_{i=1}^{n} t^s_{n,i} e^{i\omega} = \ln T^s(\omega) \qquad (4.107)$$

exists. Therefore, it is independent of cyclomatic index c. In addition, by assuming the expected asymptotic forms

$$T^s_n(\omega) \sim n^{-\Theta_0(\omega)} T^s(\omega)^n \quad , \quad A^s_n(c,\omega) \sim n^{-\Theta_c(\omega)} T^s(\omega)^n, \qquad (4.108)$$

we show that

$$\Theta_c(\omega) = \Theta_0(\omega) - c \qquad (4.109)$$

if either of them exists.

The idea of the proof is to show that by a rearrangement of the local configuration of a site animal or a site tree, we can either delete cycles from the animal or introduce a cycle to the tree at *any* vertex, which will yield two inequalities between $T^s_n(\omega)$ and $A^s_n(c,\omega)$ analogous to (4.72) and (4.94). Then by following the same approach, we also establish the existence of the limit (4.14) for site trees. Combining all these together then gives (4.107) and (4.109) for site c-animals.

4.5.1 Deleting cycles from an animal

We give a transformation to delete cycles from a c-animal. We state it as a theorem:

Theorem 4.8 *Any c-animal can be converted to a new animal such that the new animal has a cyclomatic index strictly less than c. The new animal can have at most* $(n-3)M_1$ *c-animals as its precursors for some constant* M_1.

Proof: Consider a c-animal **A** with a vertex set $\mathcal{V}$. Let $\mathbf{v}_0 = (x_0,\ y_0)$ be the bottom vertex of one cycle of **A** (the bottom vertex of the vertex set consisting of all vertices of the cycle). From the definition of the bottom vertex, $\mathbf{v}_0$ is connected to the vertices $\mathbf{v}_1$ and $\mathbf{v}_2$ with coordinates $(x_0+1,\ y_0)$ and $(x_0,\ y_0+1)$ respectively. We define a square area at $\mathbf{v}_0$ given by

$$\mathcal{S}(\mathbf{v}_0) := \{\ (x,\ y),\quad x_0 - 4 \le x \le x_0 + 4,\ y_0 \le y \le y_0 + 8\}, \tag{4.110}$$

which has the edge $[\mathbf{v}_0,\ \mathbf{v}_1]$ inside (Figure 4.2(a)). By eliminating all vertices and edges of **A** contained inside $\mathcal{S}(\mathbf{v}_0)$, therefore the edge $[\mathbf{v}_0,\ \mathbf{v}_1]$, we delete the cycle which has $\mathbf{v}_0$ as its bottom vertex, and also break **A** into a group of finite number of disconnected subclusters with each of them having at least one vertex on the boundary of $\mathcal{S}(\mathbf{v}_0)$ (Figure 4.2(b)). The number of cycles which the subclusters can have is then strictly less than c. Let $\mathcal{V}'$ be the vertex set of the subclusters.

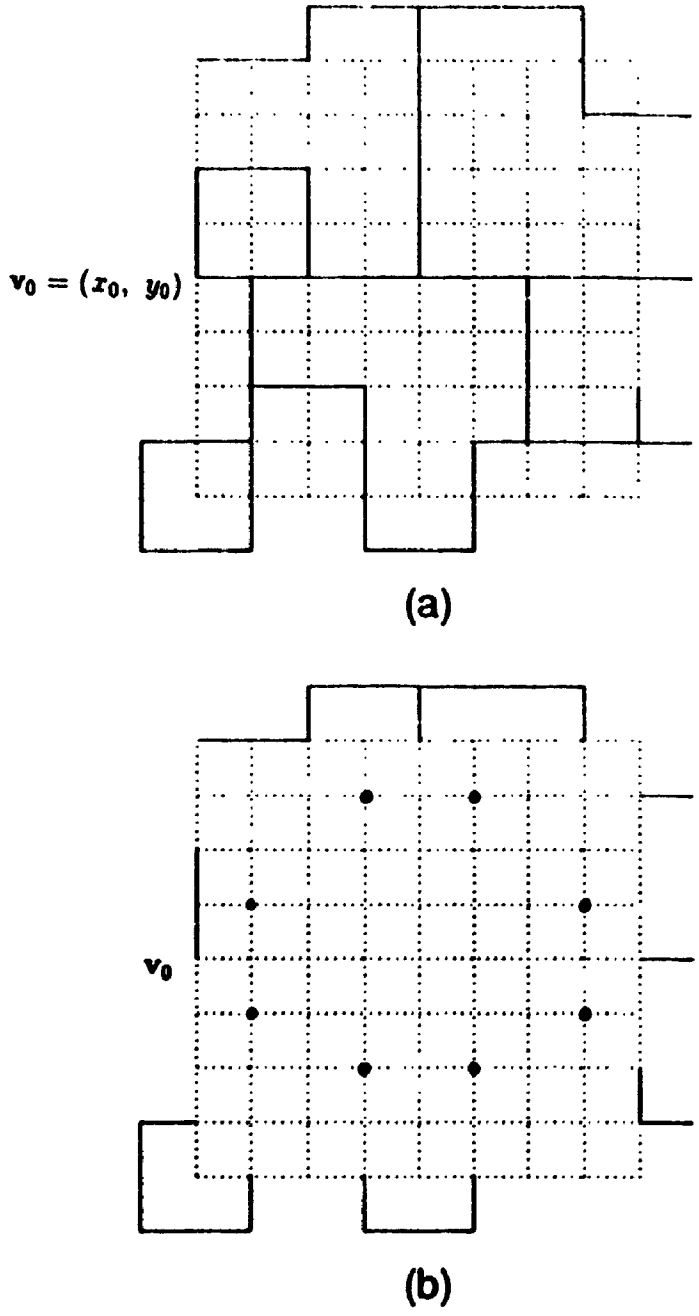


Figure 4.2: (a) The square area (dashed lines) is defined for **A** (solid lines) at $\mathbf{v}_0$; (b) Deleting all vertices and edges of **A** inside $\mathcal{S}(\mathbf{v}_0)$ breaks **A** into disconnected clusters. "•" represent lattice vertices of $\mathcal{W}$ given by (4.111).

Let $\mathcal{W}$ be the set containing eight lattice vertices:

$$\begin{aligned}\mathcal{W} =: \{&\mathbf{w}_1 = (x_0+1,\ y_0+1),\ \mathbf{w}_2 = (x_0+3,\ y_0+3), \\ &\mathbf{v}_3 = (x_0+5,\ y_0+3),\ \mathbf{w}_4 = (x_0+7,\ y_0+1), \\ &\mathbf{w}_5 = (x_0+7, y_0-1),\ \mathbf{w}_6 = (x_0+5,\ y_0-3), \\ &\mathbf{w}_7 = (x_0+3,\ y_0-3),\ \mathbf{w}_8 = (x_0-1,\ y_0-1)\}.\end{aligned} \tag{4.111}$$

For each subcluster C, let its vertex set be $\mathcal{V}(\mathbf{C})$. Then, we have $d(\mathcal{V}(\mathbf{C}), \mathcal{W}) = 1$, or 2, or 3. Especially, the subcluster containing $\mathbf{v}_0$ has a distance one with $\mathcal{W}$. We choose some vertices from each subcluster as follows:

If $d(\mathcal{V}(\mathbf{C}), \mathcal{W}) = 1$, we choose all vertices which have one step to $\mathcal{W}$. We denote by $\mathcal{V}_1$ the set for all such vertices.

If $d(\mathcal{V}(\mathbf{C}), \mathcal{W}) = 2$, we choose one and only vertex $\mathbf{v}$ from C which is two steps to either one vertex or two vertices in $\mathcal{W}$. We denote by $\mathcal{V}_2^1$ and $\mathcal{V}_2^2$ the sets for all such vertices respectively.

If $d(\mathcal{V}(\mathbf{C}), \mathcal{W}) = 3$, we choose one and only one vertex $\mathbf{v}$ which is three steps to a vertex in $\mathcal{W}$. Since in A, such a cluster C must be connected with others through one of such vertices, we also let $\mathbf{v}$ be such a vertex.

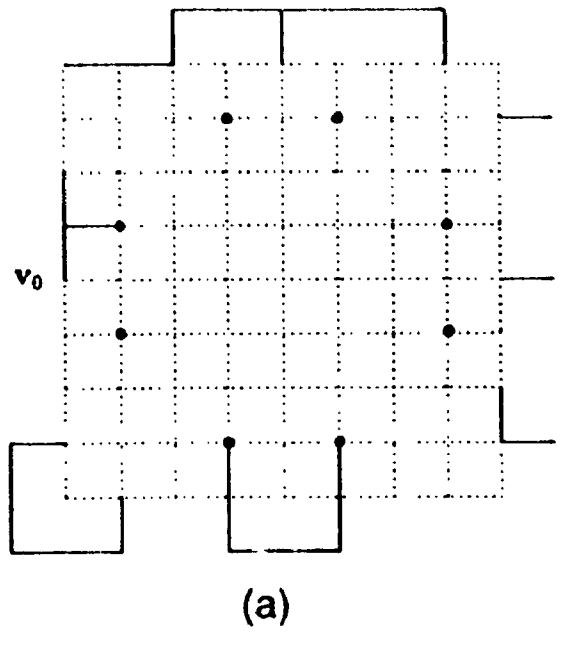
By this selection, we obtain that

(A) *If a vertex* $\mathbf{v}$ *is in* $\mathcal{V}_j$, *its nearest neighbour vertex with* $j-1$ *steps to* $\mathcal{W}$ *cannot be in* $\mathcal{V}'$.

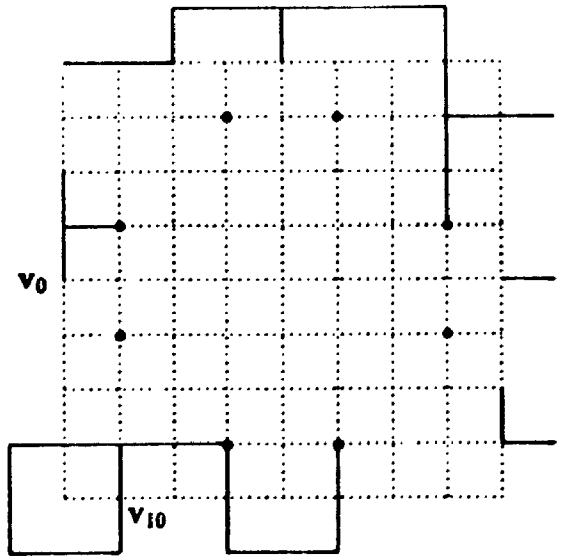
We connect each vertex in $\mathcal{V}_1$, $\mathcal{V}_2^1$, $\mathcal{V}_2^2$ and $\mathcal{V}_3$ to a vertex which coincides with some vertex in $\mathcal{W}$ (we may simply say " connect a vertex with $\mathcal{W}$ ") as follows:

(1). First, we deal with vertices in $\mathcal{V}_1$. This is simple. For each vertex $\mathbf{v} \in \mathcal{V}_1$, we add the corresponding vertex $\mathbf{w} \in \mathcal{W}$ and the edge $[\mathbf{v}, \mathbf{w}]$ (Figure 4.3 (a)).

(2). Next we consider the vertices in $\mathcal{V}_3$. Without loss of generality, we let the vertex $\mathbf{v}_{10} = (x_0+1,\ y_0-4)$ be such a vertex, therefore, in A, the cluster which $\mathbf{v}_{10}$ belongs to is connected with other clusters through $\mathbf{v}_{10}$. We add the vertex



(a)



(b)

Figure 4.3: (a) Connecting vertices in $\mathcal{V}_1$ with $\mathcal{W}$; (b) connecting vertices in $\mathcal{V}_3$ with $\mathcal{W}$.

$\mathbf{v}_{11} = \mathbf{v}_{10} + \mathbf{e}_2$ and the edge $[\mathbf{v}_{10}, \mathbf{v}_{11}]$. There are three subcases:

(i) $\mathbf{v}_{01} = (x_0, y_0 - 3)$ is in $\mathcal{V}'$ and already connected to $\mathcal{W}$. Adding the edge $[\mathbf{v}_{01}, \mathbf{v}_{11}]$ connects $\mathbf{v}_{10}$ to $\mathcal{W}$.

(ii) $\mathbf{v}_{01}$ is in $\mathcal{V}'$ and not connected to $\mathcal{W}$. We connect it with $\mathbf{v}_{11}$ and add two other vertices $\mathbf{v}_{12} = \mathbf{v}_{11} + \mathbf{e}_1$ and $\mathbf{v}_{13} = \mathbf{v}_{11} + 2\mathbf{e}_1 = \mathbf{w}_7$ and the corresponding edges. Then we remove from $\mathcal{V}_3$, $\mathcal{V}_2^1$ and $\mathcal{V}_2^2$ the vertex which is the same cluster as $\mathbf{v}_{01}$. In this case, $\mathbf{v}_{10}$ and $\mathbf{v}_{01}$ may belong to the same cluster. From the definition for the vertices in $\mathcal{V}_3$, the vertex $\mathbf{v}_{11}$ and its two incident edges are part of $\mathbf{A}$ and we have recovered a cycle of $\mathbf{A}$ which does not contain the edge $[\mathbf{v}_0, \mathbf{v}_1]$. It can be shown that the number of cycles is still strictly less than c as follows: If it is not true and there exist c cycles, clearly, none of them contains the edge $[\mathbf{v}_0, \mathbf{v}_1]$. By recovering $\mathbf{A}$, we also recover the cycle which contains the edge $[\mathbf{v}_0, \mathbf{v}_1]$. It indicates that $\mathbf{A}$ has $c + 1$ cycles, which gives a contradiction.

(iii) $\mathbf{v}_{01}$ is not in $\mathcal{V}'$. We connect $\mathbf{v}_{11}$, hence, $\mathbf{v}_{10}$ to $\mathcal{W}$ in the same way as that in case (ii).

(Figure 4.3 (b)). From this procedure, we connect all vertices in $\mathcal{V}_3$ to $\mathcal{W}$ and also have some disconnected clusters connected together. We obtain a new group of finite number disconnected clusters, which can have at most $(c - 1)$ cycles. We also obtain that

(B) *Any vertex in $\mathcal{V}_3$ is either connected with only one vertex in $\mathcal{W}$ or with more than one vertex in $\mathcal{W}$ such that each of them is connected with one vertex in $\mathcal{V}_1$.*

After (2), we have some vertices in $\mathcal{V}_2^1$ and $\mathcal{V}_2^2$ connected with $\mathcal{W}$ and removed from these two sets. For convenience, we still denote by $\mathcal{V}_2^1$ and $\mathcal{V}_2^2$ those remaining vertices which have not been connected with $\mathcal{W}$.

(3). We consider the vertices in $\mathcal{V}_2^1$ first. From the definitions of $\mathcal{V}_2^1$ and $\mathcal{W}$, we have

(C) *A vertex in $\mathcal{V}_2^1$ can only be two steps away from one vertex in $\mathcal{W}$ and also a vertex in $\mathcal{W}$ can be two steps away from one vertex in $\mathcal{V}_2^1$.*

Therefore, for such a pair, we may say that one is the other's correspondence. Consider a vertex $v_1 \in \mathcal{V}_2^1$. Add one step to it to connect with a vertex v_1' inside $\mathcal{S}(v_0)$. v_1' is then one step apart from to the correspondence, w of v_1. From (A), (C) and the procedure in (2), w cannot be connected with any vertex in $\mathcal{V}'$. It is possible that v_1' is also one step apart from a vertex v_1'' which is then connected with one vertex in $\mathcal{V}_3$, therefore, to one of the vertices in $\mathcal{W}$. In this case, we add the edge $[v_1', v_2'']$. Otherwise, we add the edge $[v_1', w]$ which connects v_1 with w. The procedure connects all vertices in $\mathcal{V}_2^1$ to $\mathcal{W}$ without creating any new cycle (Figure 4.4 (a)). We also have

(D) *Any vertex in $\mathcal{V}_2^1$ is connected either to its correspondence or some vertices in $\mathcal{W}$ other that its correspondence.*

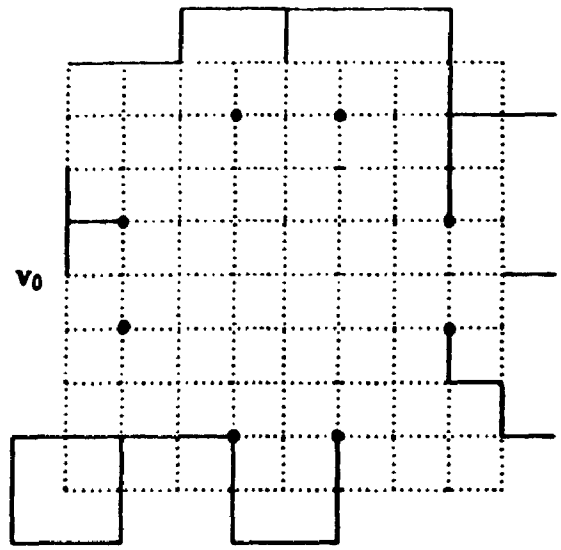
(4) Finally, we consider vertices in $\mathcal{V}_2^2$. Let v_2 be one of them. Adding the edge $[v_2, v_2']$ connects it with the vertex v_2' inside $\mathcal{S}(v_0)$ which is the nearest neighbourhood of two vertices w', w'' of $\mathcal{W}$. We have three subcases:

(i) Neither of w' and w'' is connected with any vertex in $\mathcal{V}'$, we choose any of them, say w' and add the $[v_2', w']$. In this case, w' is in the nearest neighbourhood of v_1' (given above), we also add the edge $[v_1', v_2']$.

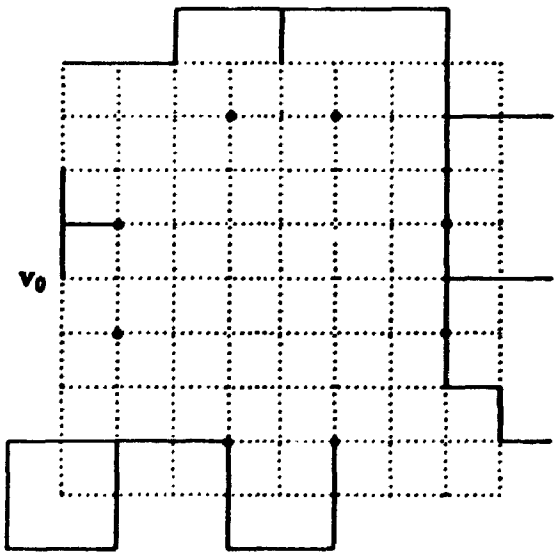
(ii) One of them, say w' is connected with a vertex in $\mathcal{V}'$, we add the edge $[v_2', w']$.

(iii). Each of them is connected with one vertex in a vertex in $\mathcal{V}'$. From (A), (B) (C) and (D), each of them can only be connected with one vertex in $\mathcal{V}_2^1$ or one vertex in $\mathcal{V}_3$ and therefore, w' and w'' are disconnected with each other. We add the edges $[v_2', w']$ and $[v_2', w'']$ to connect v_2 with $\mathcal{W}$.

(Figure 4.4 (b)). From the procedure, in each case, no new cycle can be formed.



(a)



(b)

Figure 4.4: (a) Connecting vertices in $\mathcal{V}_2^1$ with $\mathcal{W}$; (b) connecting vertices in $\mathcal{V}_2^2$ with $\mathcal{W}$.

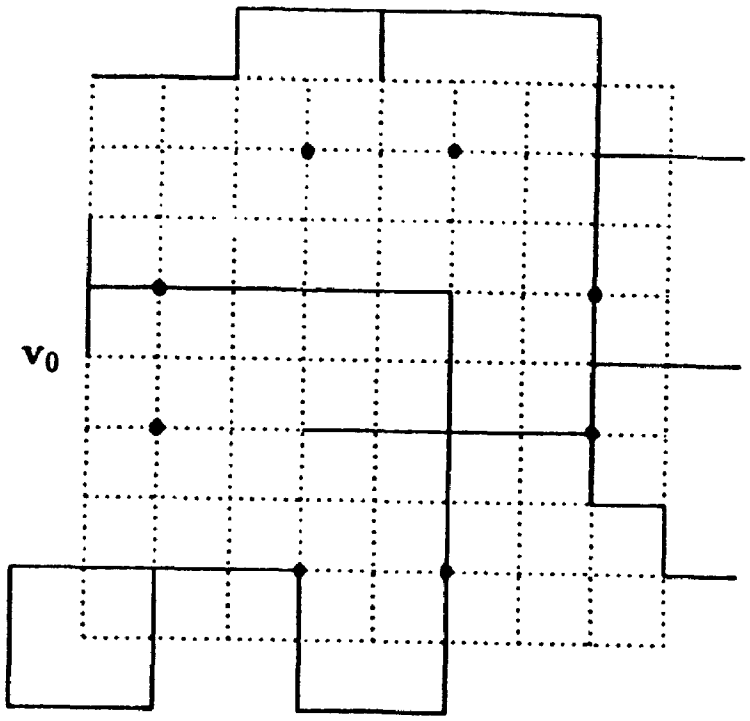


Figure 4.5: Connecting all disconnected clusters to form a new animal

Now we have connected all disconnected subclusters to some vertices in $\mathcal{W}$ and obtain some new clusters. If there is only one cluster, it indicates that we already have all clusters connected together and form a new connected cluster $\mathbf{A}'$. Otherwise, we add a 6-step walk which starts at $\mathbf{z}' = (x_0+3,\ y_0-1)$ and ends at $\mathbf{z}'' = (x_0+3,\ y_0+1)$:

$$\{\mathbf{z}',\ \mathbf{z}'+\mathbf{e}_1,\ \mathbf{z}'+2\mathbf{e}_1,\ \mathbf{z}'+2\mathbf{e}_1+\mathbf{e}_2,\ \mathbf{z}'+2\mathbf{e}_1+2\mathbf{e}_2,\ \mathbf{z}'+\mathbf{e}_1+2\mathbf{e}_2,\ \mathbf{z}''\}. \quad (4.112)$$

The walk is two steps away from each new cluster. From each disconnected cluster, we choose one vertex which is in $\mathcal{W}$, and connect it with one vertex of the walk by adding two edges. This connects all clusters to the walk and forms one connected cluster $\mathbf{A}'$. From our discussion, in either case, we obtain a new animal $\mathbf{A}'$ which has a cyclomatic index strictly less than c (Figure 4.5).

Since such a transformation changes a c-animal $\mathbf{A}$ only by its local configuration confined within $\mathcal{S}(\mathbf{v}_0)$, any two c-animals $\mathbf{A}_1$, $\mathbf{A}_2$ can yield the same new animal $\mathbf{A}'$

only if they differ from each other by the configurations inside $\mathcal{S}(\mathbf{v}_1)$ and $\mathcal{S}(\mathbf{v}_2)$, where $\mathbf{v}_1$ and $\mathbf{v}_2$ are two vertices of $\mathbf{A}_1$ and $\mathbf{A}_2$ such that $\mathbf{A}_1$ has $\mathbf{v}_1$ as the bottom vertex of one of its cycles and $\mathbf{A}_2$ has $\mathbf{v}_2$ as the bottom vertex of one of its cycles. Since, in a hypercubic lattice, at least four vertices are needed to form a cycle, an n-vertex c-animal can have at most $(n-3)$ vertices which could be the bottom vertex of a cycle. Also, within $\mathcal{S}(\mathbf{v}_0)$, the total number of configurations of c-animals is bounded above by

$$M_1 = \sum_{1\le k\le K}\sum_{0\le j\le c} a_k^s(j), \tag{4.113}$$

where $a_{k^s}(j)$ is the number of k-vertex site j-animal in the bulk. Hence, $\mathbf{A}'$ can have at most $(n-3)M_1$ c-animals as its precursors.

Within the procedure, we have deleted k_1 vertices of which j_1 are in the surface and added k_2 vertices of which j_2 are in the surface. The resulting animal $\mathbf{A}'$ has $n-k_1+k_2$ vertices with $i-j_1+j_2$ of them in the surface. Within $\mathcal{S}(\mathbf{v}_0)$, an embedding can have at most $K=7^2$ vertices with at most 7 of them in the surface, therefore, we have $\mid k \mid = \mid k_1-k_2 \mid \le K$ and $\mid j \mid = \mid j_1-j_2 \mid \le 7$. Denoting by $a_{n,i}^s(c)$ the number of animals in $\mathcal{A}_{n,i}(c)$ $(a_{n,i}^s(0)=t_{n,i}^s)$, we have

$$a_{n,i}^s(c) \le (n-3)M_1 \sum_{|k|\le K}\sum_{|j|\le 7} a_{n+k,i+j}^s(c-1)+\cdots+a_{n+k,i+j}^s(1)+t_{n+k,i+j}^s. \tag{4.114}$$

Multiplying both sides with $e^{i\omega}$ and summing over i gives

$$\begin{aligned} A_n^s(c,\omega) &\le (n-3)M_1 \sum_{|k|\le K} 14(1+2\cosh\omega+\cdots+2\cosh 7\omega) \\ &\quad [A_{n+k}^s(c-1,\omega)+\cdots+A_{n+k}^s(1,\omega)+T_{n+k}^s(\omega)] \\ &\le (n-3)M_1 14(2K)(1+2\cosh\omega+\cdots+2\cosh 7\omega) \\ &\quad [A_{n+K}^s(c-1,\omega)+\cdots+A_{n+K}^s(1,\omega)+T_{n+K}^s(\omega)]. \end{aligned} \tag{4.115}$$

By using this recursion c times, we obtain

$$A_n^s(c,\omega) \le (n-3)M_1 f(\omega) T_{n+K}^s(\omega)+\cdots$$

$$+(n-3)(n-3+K)\cdots[n-3+(c-1)K]M_1{}^c f(\omega)^c T^a_{n+cK}(\omega)$$

$$\leq c[n-3+(c-1)K]^c M_1{}^c f(\omega)^c T^a_{n+cK}(\omega) \tag{4.116}$$

with

$$f(\omega) = 14(2K)(1+2\cosh\omega+\cdots+2\cosh 7\omega). \tag{4.117}$$

4.5.2 Introducing a cycle to a tree

A lower bound on $A_n(c,\omega)$ can also be derived in the same fashion except that, in this case, we let $\mathbf{v}_0$ be any vertex of a tree. By following the same procedure, we connect all disconnected clusters to some vertices of $\mathcal{W}$. No matter how many new clusters are formed, we add a 8-cycle $\mathbf{P}$ with its bottom vertex at the vertex $\mathbf{w}_s = (x_0-1,\ y_0-1)$ and connect each disconnected clusters with $\mathbf{P}$ through one vertex which is in $\mathcal{W}$. This yields a 1-animal.

Performing such a transformation at different vertices will yield different 1-animals which differ from each other at least at the bottom vertices of added 8-cycles. Therefore, the precursors of the resulting 1-animal can only be those trees which differ with each other only by the configuration inside $\mathcal{S}(\mathbf{v}_0)$. The total number of such trees is bounded above by

$$M_2 = \sum_{k\leq K} t^a_k, \tag{4.118}$$

where t^a_k is the number of k-vertex site trees in the bulk. Therefore, the resulting 1-animal can have at most M_2 trees as its precursors. To convert $\mathbf{T}$ into a c-animal, we note that, in the above procedure, there is a neighbourhood, $\mathcal{N}(\mathbf{v}_0)$, of $\mathbf{v}_0$ defined by

$$\mathcal{N}(\mathbf{v}_0) := \{(x,\ y):\ |\ x-x_0\ |\leq 9,\ \ |\ y-y_0\ |\leq 9\} \tag{4.119}$$

such that if $\mathbf{T}$ has another vertex $\mathbf{v}_0'$ which is not in $\mathcal{N}(\mathbf{v}_0)$, repeating the same transformation at $\mathbf{v}_0'$ will leave the cycle at $\mathbf{v}_0$ unchanged. $\mathbf{T}$ can have at most

$N = (18)^4$ vertices contained in $\mathcal{N}(\mathbf{v}_0)$. Hence, if $n > (c-1)\cdot N$, there are at least

$$\binom{n}{1}\binom{n-N}{1}\cdots\binom{n-(c-1)N}{1}/c! \qquad (4.120)$$

ways to select the c vertices at which we can carry out the transformation successfully to convert $\mathbf{T}$ into a distinct c-animal. Therefore, from the above arguments, we obtain

$$\sum_{|k|\le cK}\sum_{|i|\le 7c} a^s_{n+k,i+j}(c) \ge \prod_{0\le j\le c-1}\binom{n-j\cdot N}{1} t^s_{n,i}/(M_2{}^c c!). \qquad (4.121)$$

Muliplying both sides with $e^{i\omega}$ and summing over i yields

$$\begin{aligned} &14c\sum_{|k|\le cK} A^s_{n+k}(c,\omega)(1+2\cosh\omega+\cdots+2\cosh 7c\omega) \\ &\ge \prod_{0\le j\le c-1}\binom{n-j\cdot N}{1} T^s_n(\omega)/(M_2{}^c c!), \end{aligned} \qquad (4.122)$$

or, for sufficiently large n,

$$14c^2 K A^s_{n+cK}(c,\omega) f_1(\omega) \ge n^c T^s_n(\omega)(1+o(n)), \qquad (4.123)$$

where $f_1(\omega) = (1+2\cosh\omega+\cdots+2\cosh 7c\omega)$.

By combining it with equations (4.116) and (4.134), we obtain

Theorem 4.9 a) *The limit*

$$\lim_{n\to\infty}\frac{1}{n}\ln A^s_n(c,\omega) = \ln T^s(\omega) \qquad (4.124)$$

exists and is independent of cyclomatic index c.

b) *If the limit*

$$\lim_{n\to\infty}\frac{\ln T^s_n(\omega) - n\ln T^s(\omega)}{\ln n} = -\Theta_0(\omega) \qquad (4.125)$$

exists, then

$$\lim_{n\to\infty}\frac{\ln A^s_n(c,\omega) - n\ln Ts(\omega)}{\ln n} = -\Theta_c(\omega) \qquad (4.126)$$

exists for all c *and*

$$\Theta_c(\omega) = \Theta_0(\omega) - c. \qquad (4.127)$$

4.5.3 The existence of limit (4.14) for site trees

We establish (4.14) for site trees in the square lattice. Let $\mathbf{T}_1$ be an n_1-vertex tree with i_1 vertices in the surface and $\mathbf{T}_2$ an n_2-vertex tree with i_2 vertices in the surface. By following the arguments in section 3.2.1, we can body shift $\mathbf{T}_2$ in the y direction until $d(\mathcal{V}_1,\ \mathcal{V}_2) = 2$, where $\mathcal{V}_1$ is the vertex set of $\mathbf{T}_1$ and $\mathcal{V}_2$ is the vertex set of $\mathbf{T}_2$. From theorem 4.1, there exist $\mathbf{v}_1 \in \mathcal{V}(\mathbf{T}_1)$ and $\mathbf{v}_2 \in \mathcal{V}(\mathbf{T}_2)$ such that $\mathbf{v}_2 = \mathbf{v}_1 + 2\mathbf{e}_2$. We add the vertex $\mathbf{v}_1 + \mathbf{e}_2$ and all edges to connect it with its nearest neighbour vertices contained in $\mathcal{V}_1$ and $\mathcal{V}_2$. In the square lattice, a vertex can have at most four nearest neighbour vertices. From Euler's relation (3.1), the resulting graph is an $(n_1 + n_2 + 1)$-vertex animal which can have, at most, two cycles. Any distinct pair of $\mathbf{T}_1$ and $\mathbf{T}_2$ gives a distinct such animal. Therefore, we have

$$\begin{aligned} t^s_{n_1,i_1} t^s_{n_2,i_2} \ \leq\ & t^s_{n_1+n_2+1,i_1+i_2} + t^s_{n_1+n_2,i_1+i_2+1} \\ & + a^s_{n_1+n_2+1,i_1+i_2}(1) + a^s_{n_1+n_2+1,i_1+i_2+1}(1) \\ & + a^s_{n_1+n_2+1,i_1+i_2}(2) + a_{n_1+n_2+1,i_1+i_2+1}s(2). \end{aligned} \tag{4.128}$$

Multiplying both sides with $e^{(i_1+i_2)\omega}$ and summing over $i_1 + i_2$ yields

$$\begin{aligned} T^s_{n_1}(\omega) T^s_{n_2}(\omega) \ \leq\ & \sum_{i=1}^{n_1+n_2} i[t^s_{n_1+n_2+1,i} + t^s_{n_1+n_2,i+1} \\ & + a^s_{n_1+n_2+1,i}(1) + a^s_{n_1+n_2+1,i_1+1}(1) \\ & + a^s_{n_1+n_2+1,i}(2) + a^s_{n_1+n_2+1,i+1}(2)]e^{i\omega} \\ \leq\ & (n_1 + n_2)(1 + e^{-\omega}) \\ & [T^s_{n_1+n_2+1}(\omega) + A^s_{n_1+n_2+1}(1,\omega) + A^s_{n_1+n_2+1}(2,\omega)]. \end{aligned} \tag{4.129}$$

By (4.116), we have

$$\begin{aligned} T^s_{n_1}(\omega) T^s_{n_2}(\omega) \ \leq\ & (n_1 + n_2)(1 + e^{-\omega})[T^s_{n_1+n_2+1}(\omega) \\ & + (n_1 + n_2 - 3) f(\omega) T^s_{n_1+n_2+1+K}(\omega) \\ & + (n_1 + n_2 - 3 + K)^2 f(\omega)^2 T^s_{n_1+n_2+1+2K}(\omega)], \end{aligned} \tag{4.130}$$

where $f(\omega)$ is given in (4.117).

For a tree $\mathbf{T}$ with n vertices of which i of them are in the surface, we let $\mathcal{V}'$ be the subset of its vertex set such that $\mathcal{V}'$ contains all vertices of degree 1 except the one rooted at 0. Then, by deleting the top vertex in $\mathcal{V}'$, we convert the n-vertex tree into an $(n-1)$-vertex tree which has either i or $i-1$ vertices in the surface. The new tree can have at most n n-vertex trees as its precursors which differ only at the top vertex of $\mathcal{V}'$. Then by repeating the same procedure K times, we obtain an $(n-K)$-vertex tree, which can have at most $n(n-1)\cdots(n-K+1)$ n-vertex trees as its precursors. Hence, we have

$$t^s_{n,i} \le n(n-1)\cdots(n-K+1)(t^s_{n,i-K}+\cdots+t^s_{n,i}). \tag{4.131}$$

Multiplying both sides with $e^{i\omega}$ and summing over i yields

$$\begin{aligned} T^s_n(\omega) &\le n(n-1)\cdots(n-K+1)K(1+e^{|\omega|}+\cdots+e^{K|\omega|})T^s_{n-K}(\omega) \\ &\le n^K g_K(\omega)T^s_{n-K}(\omega), \end{aligned} \tag{4.132}$$

where $g_K(\omega) = K(1+e^{|\omega|}+\cdots+e^{K|\omega|})$. Substituting it in (4.130) gives

$$\begin{aligned} T^s_{n_1}(\omega)T^s_{n_2}(\omega) &\le (n_1+n_2)(1+e^{-\omega})\{(n_1+n_2+1)g_1(\omega)T^s_{n_1+n_2}(\omega) \\ &\quad +(n_1+n_2-3)(n_1+n_2+1+K)^{K+1}g_{K+1}(\omega)f(\omega)T^s_{n_1+n_2}(\omega) \\ &\quad +(n_1+n_2+K)^2(n_1+n_2+1+2K)^{2K+1}g_{2K+1}(\omega)f(\omega)^2T^s_{n_1+n_2}(\omega)\} \\ &\le 3(n_1+n_2+1+2K)^{2K+4}g_{2K+1}(\omega)f(\omega)^2T^s_{n_1+n_2}(\omega). \end{aligned} \tag{4.133}$$

Since $\sum_{n=1}^{\infty} n^{-2}\ln(n+K)$ is a convergent series and $-\frac{1}{n}\ln T^s_n(\omega) \ge -\frac{1}{n}(\ln nt^s_n + n\omega) \ge -(\ln\Lambda_0+\omega+1)$, by theorem 4.2, we establish the existence of the limit

$$\lim_{n\to\infty}\frac{1}{n}\ln T^s_n(\omega) = \ln T^s(\omega) \tag{4.134}$$

for site trees in the square lattice.

4.5.4 Discussion

By using a different approach from that for bond embeddings in section 4.4, we establish analogous results (4.97) and (4.100) for site embeddings in the square lattice. But we do not have a clear idea of how to extend such an approach to site embeddings in a lattice with a dimensionality greater than two (one thing for sure is that we should replace the square $S(v_0)$ by an appropriate hypercube). The difficulty is when we connect all disconnected clusters together by following the above procedure We do not know how to avoid cycles that are not needed.

However, for bond embeddings, there is no such difficulty since by the definition of a bond embedding, any two vertices which are in contact may not be connected by an edge. Therefore, the procedure of introducing a cycle to *any* vertex of an embedding can be applied to bond embeddings in any d-dimensional lattice, which immediately yields an inequality analogous to (4.94) for bond embeddings by counting either the number of vertices or the number of edges in the surface. By using this inequality with the inequality (4.103), we prove theorem 4.7 for n-edge bond c-animals.

4.6 Numerical estimates of the transition point

The generating function of the partition function (4.12) is given by

$$G(x,y) = \sum_{n,m} t_{n,m} x^{n-m} y^m, \tag{4.135}$$

where $t_{n,m}$ is the number of distinct lattice tree (weak) embeddings rooted at the surface with m surface contacts. We consider both the case where m is the number of tree vertices in the surface and the case where m is the number of tree edges in the surface. The data analyzed are given in reference [59].

Two methods are used to analyze the generating function $G(x,y)$. In the first method the problem is reduced to a one variable analysis by analyzing the data at a series of fixed values of $r = y/x$. $D-log$ Padé appoximants to the resulting series in

x are then used to estimate the critical value of x for the given value of y. We have considered both the cases of penetrable and impenetrable surfaces.

In the penetrable surface problem we expect the adsorption transition to occur at $y = y_c = x_c$. Although this result has not been established rigorously it is indicated by noting that when $y = x$ the problem is just the bulk lattice tree problem and therefore the dominant critical behaviour has an associated critical exponent which is just the bulk exponent θ. From this we identify the crossover point at which the surface adsorption occurs to be at $y_c = x_c$. The difficulty with verifying this from the one variable analysis described above is that while the value of x_c should be a constant for $r \leq r_c = y_c/x_c$, a plot of x_c vs y through a range of values of r shows that the estimate of x_c varies continuously for a wide range of r values. This is common to this one variable type of analysis (De'Bell and Essam [42]). We therefore attempted to estimate the value of r at which the downward curvature of the x_c estimates rapidly increased using this as our best estimate of r_c. In all cases the results obtained in this way are consistent with $r_c = 1$ for the penetrable surface.

By analogy with the results obtained for the penetrable surface, we estimate r_c for the impenetrable surface by locating the value of r at which the estimates of x_c consistently fall below the known bulk value. The values of r_c obtained in this way are presented in Table 4.1. The bulk values of x_c used are those obtained by the Baker-Hunter confluent singularity method as described in section 2.2. A plot of x_c versus r for the triangular lattice with an impenetrable surface and surface contacts counted by the number of tree edges in the surface is shown in figure 1. Corresponding plots for the other problems considered are similar but, in general, the approximants are less well behaved.

The second method is the partial differential approximant method (PDA) introduced in section 2.2. We find that the estimates of $(x_c,\ r_c)$ obtained are rather scattered. However, as described for the self avoiding walk problem, the scattered

Table 4.1: Summary of critical points (x_c, y_c) for the surface-adsorption transition. x_c values are those obtained by applying the Baker-Hunter method to the bulk series. y_c values in the second column are obtained analyzing the series at fixed value of $r = y/x$; those in the third column are obtained by partial differential approximant method.

Lattice	x_c	y_c/x_c	y_c/x_c (PDA)
Triangular			
Bond	0.11892 ± 0.00001	4.35 ± 0.05	4.4 ± 0.1
Site	0.11892 ± 0.00001	2.70 ± 0.04	3.0 ± 0.2
Square			
Bond	$0.19445^{+0.00001}_{-0.00002}$	2.865 ± 0.005	2.8 ± 0.1
Site	$0.19445^{+0.00001}_{-0.00002}$	2.270 ± 0.005	2.3 ± 0.2
Simple cubic			
Bond	$0.09481^{+0.00003}_{-0.00001}$	1.51 ± 0.01	1.40 ± 0.2
Site	$0.09481^{+0.00003}_{-0.00001}$	1.47 ± 0.02	

points in the vicinity of the critical point are expected to fall on the critical lines of the phase diagram. Inspection of the estimates for the tree problems does, indeed, show them to have the expected qualitative form of the phase diagram. The values of (x_c, r_c), tabulated in Table 4.1, are obtained by plotting x_c versus r_c from various individual PDA solutions and assuming that the value of r_c at which x_c fell below its bulk value was the best estimate of r_c. The estimates of x_c, r_c from individual PDAs are superimposed on Figure 4.6 for comparison.

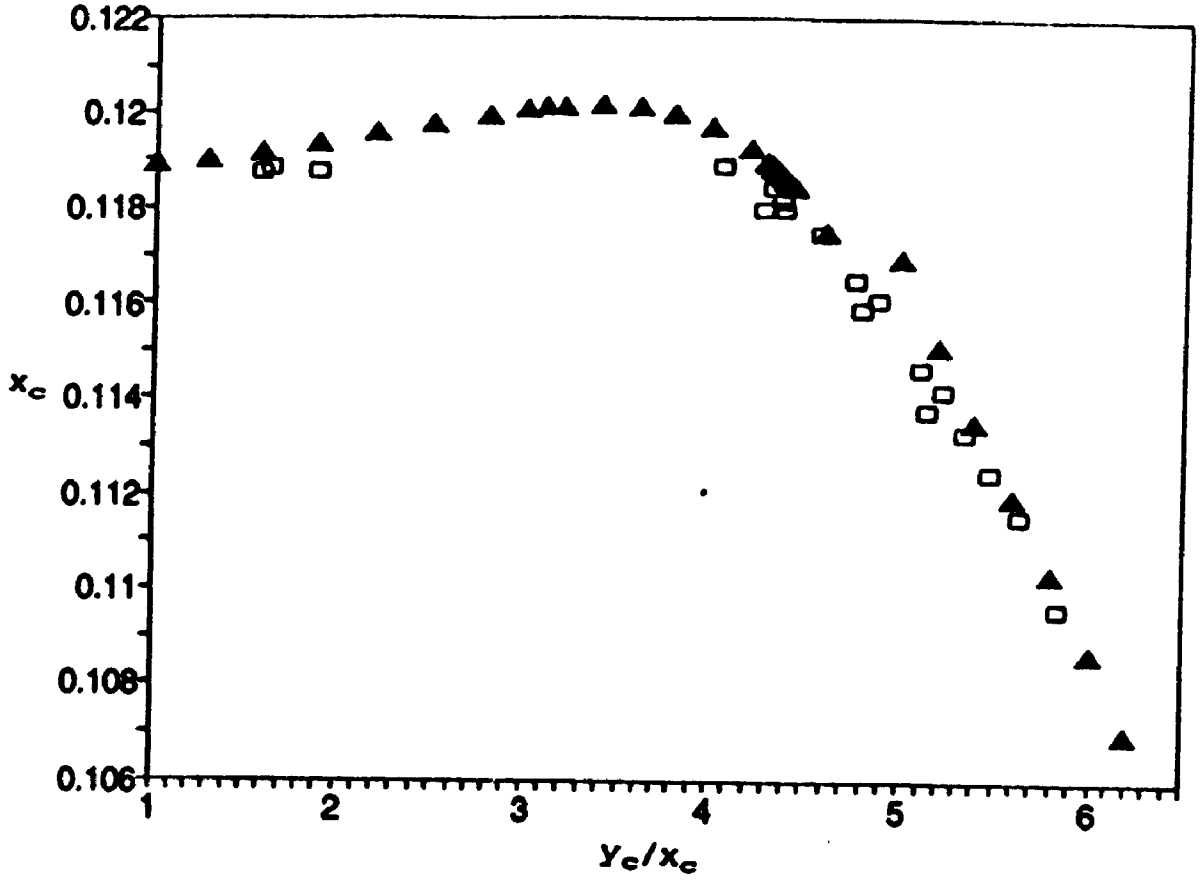


Figure 4.6: Variation of x_c with y_c/x_c for the triangular lattice with an impenetrable surface (edge problem). Solid triangle represents the x_c obtained from a typical Padé approximant ([5/5]). Open square represents the results obtained from partial differential approximants.

Chapter 5

Summary

We have used rigorous and numerical methods to study the interaction of polymers with two different types of surfaces. By following the work of Hammersley *et al* [32], we have shown the existence of the adsorption transition for branched polymers. The transition points and crossover exponents for SAWs have been numerically estimated by two-variable and one-variable analyses of exact enumeration data.

For a polymer network with a fixed topology in a $d(\geq 3)$ dimensional lattice, we have proved that the reduced free energy is the same as that for self-avoiding walks and therefore, independent of the topology. For $d = 2$, the reduced free energy depends on the topology of a network. However, we have given two examples to show that if the reduced free energy exists, even though it may differ from that of SAWs, it still has the same transition point and the same crossover exponent as that for SAWs. For lattice animals, the results of Soteros and Whittington [22] for bond c-animals have been generalized to the case where an adsorption surface exists. The same results have also been obtained for site c-animals in the square lattice. We have thus shown that for specified polymer networks and lattice animals, certain critical properties of polymers in the bulk are preserved when the polymers interact with an adsorption surface. This implies that a surface interaction is an irrelevant operator.

By using Kesten's pattern theorem [54], we have obtained a rigorous result for the exponent of twin-tailed tadpoles by relating it to the exponent of self-avoiding walks

(see equation (3.2)). This, to our knowledge, is the first nontrivial rigorous result of the exponents for polymer networks with fixed topology. It may also be possible to show that the twin-tailed tadpoles have the same exponent ν as that for SAWs given in (1.8) and (1.9). The model of twin-tailed tadpoles is also relevant to the study of polymer trails which are random walks on a lattice with a less restrictive self-avoiding constraint than that for SAWs. These problems are currently under investigation.

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