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Statistics of collapsing lattice animals

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Abstract. We consider several lattice models of branched polymers in dilute solution in which the polymer molecule is modelled as a tree or animal. In general the thermodynamic properties of the polymer are determined by monomer–monomer and monomer–solvent interactions. We examine a two-variable model which incorporates both types of interaction and discuss its relationship to other models which have previously been investigated. In particular, we discuss the collapse transition in these models.

1. Introduction

Linear polymer molecules in dilute solution are expanded objects under good solvent conditions and can be conveniently modelled as self-avoiding walks on lattices. If the solvent quality is decreased the linear polymer can undergo collapse from a random coil to a ball or globule and this phenomenon has been investigated experimentally by light scattering (Slagowski *et al* 1976, Sun *et al* 1980) and by viscosity measurements (Sun *et al* 1990). A convenient model for this system is a self-avoiding walk with an energy term proportional to the number of first-neighbour *contacts*, i.e. the number of pairs of vertices of the walk which are one lattice space apart but not connected by an edge of the walk (Mazur and McCrackin 1968, Finsky *et al* 1975, Saleur 1986, Meirovitch and Lim 1989 and many other papers).

One would expect a similar collapse phenomenon in randomly branched polymers in dilute solution (as the quality of the solvent is decreased) but this does not seem to have been studied experimentally. However, a number of models of branched polymers have been considered, and there is substantial numerical evidence for the existence of a collapse transition (Derrida and Herrmann 1983, Dickman and Shieve 1984, 1986, Lam 1987, 1988, Chang and Shapir 1988, Gaunt and Flesia 1990, Flesia and Gaunt 1992). All of these models are based on either lattice trees or lattice animals and the transition is associated with a change in a fugacity controlling either the number of contacts in the tree or animal, or the cyclomatic index of the animal. Madras *et al* (1988, 1990) have derived rigorous bounds on the behaviour of the free energy for several of these models.

The behaviour of a branched polymer molecule is determined by both monomer–monomer (2–2) and solvent–monomer (1–2) interactions. Both terms can be incorporated into the model. In the *contact model* (see for instance Gaunt and Flesia (1990) and Madras *et al* (1990)) the (2–2) interactions are explicitly included but (1–2) interactions are ignored, so

that the energy term is an *effective* monomer–monomer interaction, reflecting the difference between (2–2) and (1–2) interactions. Similarly in the *solvent model* (see for instance Flesia *et al* (1992a) and Flesia (1993)) only (1–2) interactions are explicitly included.

In section 2 we define a *two-variable* model incorporating both solvent–monomer and monomer–monomer terms, and prove some results about the general properties of the free energy, including a connection with percolation theory. A preliminary account of some of this work has appeared in Flesia *et al* (1992b), and is related to the work of Coniglio (1983). In section 3 we discuss the relationship of this two-variable model to other models which have been previously studied in the literature. In section 4 we derive some bounds on the behaviour of the free energy of the two-variable model and in section 5 we concentrate on the solvent model, presenting numerical estimates of the free energy and heat capacity, and comparing these to the properties derived in section 2 and the bounds of section 4.

A related problem in which a collapse transition occurs is vesicles (Lipowsky 1991) subject to a pressure difference across their boundary. In two dimensions a vesicle is a self-avoiding polygon and its enclosed area, while a three dimensional vesicle is a closed surface homeomorphic to a sphere, and its enclosed volume. These problems have been studied by Fisher *et al* (1991), Banavar *et al* (1991), Stella *et al* (1992), Vanderzande (1993) and Whittington (1993). One can define a grand canonical ensemble by associating a fugacity, x , with the size of the boundary and a fugacity, y , with the size of the enclosed volume. The grand partition function converges in a region of the xy -plane bounded by the curve $y = y_c(x)$ and this boundary has a point of non-analyticity corresponding to a collapse transition in the vesicle. Stella *et al* and Vanderzande have suggested that this transition is closely related to the collapse transition in lattice animals. In particular, they noticed that vesicles can be mapped by a duality transformation into a particular subset of strongly embeddable lattice animals. However, this subset is exponentially small in the set of all strongly embeddable animals. In addition, Flesia *et al* (1993) have shown that the thermodynamics of the vesicle model and the corresponding model for all strongly embeddable animals are qualitatively different. In section 6 we present some additional results about the relationship between the vesicle model and the solvent model for strongly embeddable animals.

2. A generalized model

In this section we discuss a generalized model which incorporates monomer–solvent interaction terms as well as monomer–monomer terms. We consider animals weakly embeddable in the d -dimensional hypercubic lattice and restrict ourselves to site counting. Consider an animal with n vertices, cyclomatic index c , and e edges. These three quantities are related through Euler's relation

$$c = e - n + 1. \quad (2.1)$$

If a pair of vertices in the animal are near-neighbours on the lattice and are not incident on a common edge, we call this pair of vertices a *contact*. Let the number of contacts in the animal be k . If an edge of the lattice is not an edge of the animal but is incident on exactly one vertex in the animal we call this edge a *solvent contact* and write s for the number of solvent contacts associated with the animal. Clearly $s + k$ is the usual edge perimeter of the animal. Counting edges gives the relation

$$2dn = 2e + 2k + s \quad (2.2)$$

and, using (2.1)

$$s + 2k + 2c = 2(d - 1)n + 2. \tag{2.3}$$

Let $a_n(s, k)$ be the number (per lattice site) of animals with n vertices, k contacts and s solvent contacts. We define a partition function

$$Z_n(\beta_1, \beta_2) = \sum_{s,k} a_n(s, k) e^{\beta_1 s + \beta_2 k}. \tag{2.4}$$

By a concatenation argument we obtain the inequality

$$\sum_{s_1, k_1} a_{n_1}(s_1, k_1) a_{n_2}(s - s_1 + 2, k - k_1) \leq a_{n_1+n_2}(s, k). \tag{2.5}$$

Since $a_n^{1/n}$ is bounded above (Whittington and Soteros 1990) then $Z_n(\beta_1, \beta_2)^{1/n}$ is bounded above for β_1 and β_2 less than infinity. This together with equation (2.5) implies the existence of the limit

$$\lim_{n \rightarrow \infty} n^{-1} \log Z_n(\beta_1, \beta_2) = G(\beta_1, \beta_2). \tag{2.6}$$

Using Cauchy's inequality

$$\begin{aligned} Z_n(\beta_1, \beta_2) Z_n(\beta'_1, \beta'_2) &= \left(\sum_{s,k} a_n(s, k) e^{\beta_1 s + \beta_2 k} \right) \left(\sum_{s,k} a_n(s, k) e^{\beta'_1 s + \beta'_2 k} \right) \\ &\geq \left[\sum_{s,k} a_n(s, k) \exp\left(\frac{\beta_1 + \beta'_1}{2} s + \frac{\beta_2 + \beta'_2}{2} k \right) \right]^2 \\ &= \left[Z_n\left(\frac{\beta_1 + \beta'_1}{2}, \frac{\beta_2 + \beta'_2}{2} \right) \right]^2 \end{aligned} \tag{2.7}$$

so that $Z_n(\beta_1, \beta_2)^{1/n}$ is log-convex. Since the limit, when it exists, of a sequence of convex functions is itself convex it follows from equation (2.6) that $G(\beta_1, \beta_2)$ is a convex function of β_1 and β_2 . Since $G(\beta_1, \beta_2)$ is bounded above (except for β_1 or $\beta_2 = \infty$), convexity implies continuity for $\beta_1, \beta_2 < \infty$.

Since equation (2.3) gives a relationship between c, k and s we can derive a relationship between any pair of the three two-variable partition functions. For instance, if we write $a'_n(s, c)$ for the number of lattice animals with n vertices, s solvent contacts and cyclomatic index c , then we can define

$$Z'_n(\beta_1, \beta_2) = \sum_{s,c} a'_n(s, c) e^{\beta_1 s + \beta_2 c} \tag{2.8}$$

which is related to $Z_n(\beta_1, \beta_2)$ by

$$Z_n(\beta_1, \beta_2) = e^{-\beta_2((d-1)n+1)} Z'_n(\beta_1 - \frac{1}{2}\beta_2, -\beta_2). \tag{2.9}$$

The corresponding relationship between the free energies is therefore

$$G(\beta_1, \beta_2) = -(d - 1)\beta_2 + G'(\beta_1 - \frac{1}{2}\beta_2, -\beta_2). \tag{2.10}$$

As discussed in Flesia *et al* (1992b), there is an interesting connection with percolation theory. Consider the edge percolation problem with edge occupation probability p . Let $P_n(p)$ be the probability that the cluster containing the origin consists of n vertices, at edge occupation probability p . Then

$$P_n(p) = n \sum_{s,k} a_n(s, k) p^e (1 - p)^{s+k} = n p^{dn} Z_n(\beta_1, \beta_2) \tag{2.11}$$

where $e^{\beta_1} = (1-p)/\sqrt{p}$ and $e^{\beta_2} = (1-p)/p$. It is known that $\lim_{n \rightarrow \infty} n^{-1} \log P_n(p) < 0$ for $p < p_c$ and $\lim_{n \rightarrow \infty} n^{-1} \log P_n(p) = 0$ for $p > p_c$ (see for instance Grimmett 1989). Restating these results in terms of G we have, for $\beta_1 = \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$ and $\beta_2 > \log[(1-p_c)/p_c]$

$$G(\beta_1, \beta_2) < d \log(1 + e^{\beta_2}). \quad (2.12)$$

For $\beta_1 = \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$ and $\beta_2 < \log[(1-p_c)/p_c]$

$$G(\beta_1, \beta_2) = d \log(1 + e^{\beta_2}). \quad (2.13)$$

This implies that the point $(\beta_1^c, \beta_2^c) = (\log[(1-p_c)/\sqrt{p_c}], \log[(1-p_c)/p_c])$ is a singular point of the function G at least when approached along the curve $\beta_1 = \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$. For the square lattice $\beta_1^c = -\log \sqrt{2} = -0.34657 \dots$ and $\beta_2^c = 0$.

Making the usual conjecture (Grimmett 1989, page 150) that

$$P_n(p_c) \sim n^{-1-1/\delta} \quad (2.14)$$

as $n \rightarrow \infty$, we see that

$$Z_n(\beta_1^c, \beta_2^c) \sim n^{-2-1/\delta} p_c^{-dn} \quad (2.15)$$

and

$$G(\beta_1^c, \beta_2^c) = -d \log p_c. \quad (2.16)$$

In particular, for the square lattice

$$Z_n(-\log \sqrt{2}, 0) \sim n^{-187/91} 4^n \quad (2.17)$$

and $G(-\log \sqrt{2}, 0) = \log 4$.

Most of the results discussed in this section are concerned with the limiting free energy $G(\beta_1, \beta_2)$. This quantity has the disadvantage from a numerical point of view that any singular behaviour is difficult to detect. It is convenient to define a heat capacity

$$C_n(\beta_1, \beta_2) = n^{-1} [(\langle \beta_1 s + \beta_2 k \rangle)_n^2 - \langle \beta_1 s + \beta_2 k \rangle_n^2] \quad (2.18)$$

which should show peaks for small n corresponding to singular behaviour in the infinite n limit. We have calculated $C_n(\beta_1, \beta_2)$ for small values of n for the square lattice using exact enumeration data given in Madras *et al* (1990) with additional data due to Martin and Sykes (1992). In figure 1 we show the dependence on β_1 and β_2 for $n = 21$ for the square lattice. This figure shows three ridges meeting at a point close to $(-\log \sqrt{2}, 0)$, consistent with the suggestion of Flesia *et al* (1992b) that the model has three phase boundaries meeting at a triple point.

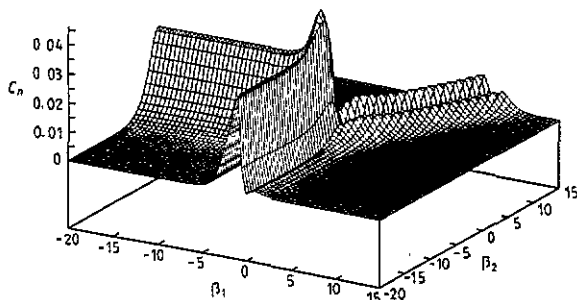


Figure 1. The heat capacity of the two-variable model for $n = 21$.

3. Connections with one-variable models

By choosing particular values for the parameters β_1 and β_2 we can recover the single variable models such as those considered in Madras *et al* (1990), Gaunt and Flesia (1990) and Flesia (1993). For instance $Z_n(0, \beta)$ is the partition function of the *contact model* and $Z_n(\beta, 0)$ is the partition function of the *solvent model* in which we have a fugacity conjugate to the solvent perimeter. We discuss this model in section 5.

The connection between the two-variable model and other one variable models is less obvious than for the contact and solvent models. To obtain the *cycle model* we note that

$$2c = 2(d - 1)n + 2 - (s + 2k). \tag{3.1}$$

If we choose $\beta_2 = 2\beta_1 = -\beta$ then

$$\beta_1 s + \beta_2 k = -[(d - 1)n + 1]\beta + c\beta \tag{3.2}$$

so that

$$Z_n(-\beta/2, -\beta) = e^{-[(d-1)n+1]\beta} Z_n^o(\beta) \tag{3.3}$$

where $Z_n^o(\beta)$ is the partition function of the cycle model. This implies that the cycle model corresponds to the line $\beta_2 = 2\beta_1$ in the (β_1, β_2) plane.

We can obtain the p -model in which the fugacity is associated with the number of pairs of nearest-neighbour vertices in the animal, whether or not they are connected by an edge. We write $p = e + k$ so that

$$p = dn - s/2 \tag{3.4}$$

and we obtain the p -model by setting $\beta_1 = -\beta/2$ and $\beta_2 = 0$, i.e. by mapping it into the solvent model. Hence the properties of the p -el are completely determined by the solvent model. The same argument applies for the p -el for strongly embeddable animals which has been studied by Derrida and Herrmann (1983). In fact for strongly embeddable animals the p -el, the cycle model and solvent model can be mapped one into another.

We can also define an *edge perimeter model* in which the fugacity is associated with the edge perimeter which appears in percolation problems, i.e. $s + k$. The appropriate partition function is

$$Z_n(\beta, \beta) = \sum_{k,s} a_n(s, k) e^{(s+k)\beta} \tag{3.5}$$

corresponding to the line $\beta_2 = \beta_1$.

An advantage of the two-variable model is that many one variable models appear as special cases and they can be studied in a unified way by studying the properties of the two-variable model.

Some other one variable lattice animal models, such as the solvent model for weakly embeddable trees and the solvent model for strongly embeddable animals, are not special cases of the two-variable model but are relevant to the behaviour of the two-variable model as β_2 goes to plus or minus infinity. In fact, in the next section we derive bounds for the limiting free energy of the two-variable model in terms of the limiting free energies of these one variable models.

4. Bounds on the free energy

There are numerous ways to obtain bounds on $G(\beta_1, \beta_2)$. One can for example, obtain bounds from combinatorial inequalities involving the $a_n(s, k)$, from maximizing or

minimizing the $e^{\beta_1 s + \beta_2 k}$ factor in the summand of $Z_n(\beta_1, \beta_2)$, from the fact that $G(\beta_1, \beta_2)$ is a convex, non-decreasing function of β_1 and β_2 or by exploiting the connections between lattice animals and percolation clusters.

In this section we discuss some examples of upper and lower bounds on $G(\beta_1, \beta_2)$.

We begin by discussing some bounds which can be obtained from a combinatorial inequality involving $a_n(s, k)$. We can derive an inequality for $a_n(s, k)$ by an extension of an argument of Madras *et al* (1988, 1990), giving

$$\binom{(d-1)n+1-k-s/2}{j} a_n(s, k) \leq \binom{k+j}{j} a_n(s, k+j) \leq \binom{dn-k-s/2}{j} a_n(s, k). \quad (4.1)$$

This inequality allows us to derive two sets of upper and lower bounds for $G(\beta_1, \beta_2)$. One set is in terms of the free energy of the solvent model for strongly embeddable animals ($k = 0$) and the other is in terms of the free energy of the solvent model for trees ($k = (d-1)n - s/2 + 1$). We expect that the first set of bounds will be important in the $\beta_2 < 0$ region where the average value of k will be near 0.

To obtain the first set of bounds we define the solvent partition function for strongly embeddable animals, $A_n(\beta)$, to be

$$A_n(\beta) = \sum_s a_n(s, 0) e^{\beta s} \quad (4.2)$$

and define the corresponding limiting free energy, $\hat{F}(\beta)$, to be

$$\hat{F}(\beta) = \lim_{n \rightarrow \infty} n^{-1} \log A_n(\beta). \quad (4.3)$$

Setting k equal to zero in equation (4.1), multiplying throughout by $e^{\beta_1 s + \beta_2 j}$ and summing over s and j gives

$$(1 + e^{\beta_2})^{(d-1)n+1} A_n(\beta) \leq Z_n(\beta_1, \beta_2) \leq (1 + e^{\beta_2})^{dn} A_n(\beta) \quad (4.4)$$

where

$$\beta = \beta_1 - \frac{1}{2} \log(1 + e^{\beta_2}). \quad (4.5)$$

Taking the appropriate limit gives the first set of upper and lower bounds,

$$(d-1) \log(1 + e^{\beta_2}) + \hat{F}(\beta) \leq G(\beta_1, \beta_2) \leq d \log(1 + e^{\beta_2}) + \hat{F}(\beta). \quad (4.6)$$

In a similar way we can derive bounds on $G(\beta_1, \beta_2)$ in terms of the free energy of the solvent model for trees. If the animal is a tree the number of cycles is identically zero and hence the number of contacts is $(d-1)n - s/2 + 1$ so that the solvent partition function for trees is given by

$$T_n(\beta) = \sum_s a_n(s, (d-1)n - s/2 + 1) e^{\beta s} \quad (4.7)$$

and the corresponding limiting free energy is

$$\mathcal{T}(\beta) = \lim_{n \rightarrow \infty} n^{-1} \log T_n(\beta). \quad (4.8)$$

Setting $k = (d-1)n - s/2 + 1 - j$ in equation (4.1), multiplying throughout by $e^{\beta_1 s + \beta_2 [(d-1)n - s/2 + 1 - j]}$ and summing over s and j leads to

$$\binom{dn}{n-1}^{-1} (1 + e^{\beta_2})^{(d-1)n+1} T_n(\beta) \leq Z_n(\beta_1, \beta_2) \leq (1 + e^{\beta_2})^{(d-1)n+1} T_n(\beta) \quad (4.9)$$

where

$$\beta = \beta_1 - \frac{1}{2} \log(1 + e^{\beta_2}). \tag{4.10}$$

Taking the appropriate limit gives the second set of upper and lower bounds

$$\begin{aligned} (d - 1) \log(1 + e^{\beta_2}) + (d - 1) \log(d - 1) - d \log d + T(\beta) &\leq G(\beta_1, \beta_2) \\ &\leq (d - 1) \log(1 + e^{\beta_2}) + T(\beta). \end{aligned} \tag{4.11}$$

Equation (4.1) can also be used to obtain a relationship between $T(\beta)$ and $\hat{F}(\beta)$. Setting $k = 0$ and $j = (d - 1)n + 1 - s/2$ in equation (4.1) and performing the appropriate operations gives

$$\hat{F}(\beta) \leq T(\beta) \leq d \log d - (d - 1) \log(d - 1) + \hat{F}(\beta). \tag{4.12}$$

Using equation (4.12) to compare equations (4.6) and (4.11) results in the combined bounds

$$\begin{aligned} (d - 1) \log(1 + e^{\beta_2}) + \hat{F}(\beta) &\leq G(\beta_1, \beta_2) \\ &\leq \begin{cases} \min\{d \log(1 + e^{\beta_2}) + \hat{F}(\beta), (d - 1) \log(1 + e^{\beta_2}) + T(\beta)\} & \beta_2 < \log\left(\frac{d^d}{(d-1)^{d-1}} - 1\right) \\ (d - 1) \log(1 + e^{\beta_2}) + T(\beta) & \beta_2 \geq \log\left(\frac{d^d}{(d-1)^{d-1}} - 1\right). \end{cases} \end{aligned} \tag{4.13}$$

Equation (4.13) can be used to obtain further bounds on $G(\beta_1, \beta_2)$ from known bounds on $\hat{F}(\beta)$ and $T(\beta)$.

The connection with percolation can also be exploited to obtain bounds on G . Since $G(\beta_1, \beta_2)$ is a non-decreasing function in β_1 and β_2 we can extend (2.12) to show that for any fixed $\beta_2 > \log[(1 - p_c)/p_c]$ and any $\beta_1 \leq \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$

$$G(\beta_1, \beta_2) < d \log(1 + e^{\beta_2}). \tag{4.14}$$

In addition, using (2.13), for any fixed $\beta_2 < \log[(1 - p_c)/p_c]$ and any $\beta_1 \leq \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$

$$G(\beta_1, \beta_2) \leq d \log(1 + e^{\beta_2}) \tag{4.15}$$

while for any $\beta_1 \geq \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$

$$G(\beta_1, \beta_2) \geq d \log(1 + e^{\beta_2}). \tag{4.16}$$

If we solve for p in terms of β_1 instead of β_2 we have

$$p = 1 + \frac{e^{2\beta_1}}{2} - \frac{e^{\beta_1} \sqrt{e^{2\beta_1} + 4}}{2} \tag{4.17}$$

and hence the curve corresponding to percolation in the (β_1, β_2) plane is

$$\beta_2 = \beta_1 + \log\left(\frac{e^{\beta_1}}{2} + \frac{\sqrt{e^{2\beta_1} + 4}}{2}\right) \tag{4.18}$$

and we can obtain bounds for fixed β_1 similar to those already derived for fixed β_2 . For example we get for fixed $\beta_1 < \log[(1 - p_c)/\sqrt{p_c}]$

$$G(\beta_1, \beta_2) \geq -d \log\left[1 + \frac{e^{2\beta_1}}{2} - \frac{e^{\beta_1} \sqrt{e^{2\beta_1} + 4}}{2}\right] \tag{4.19}$$

provided that

$$\beta_2 \geq \beta_1 + \log\left(\frac{e^{\beta_1}}{2} + \frac{\sqrt{e^{2\beta_1} + 4}}{2}\right). \tag{4.20}$$

An important lower bound can be obtained using the fact that for any choice of s and k ,

$$a_n(s, k)e^{\beta_1 s + \beta_2 k} \leq Z_n(\beta_1, \beta_2). \tag{4.21}$$

If we choose $(s, k) \in \{(2(d-1)n + 2, 0), (s_{\min}, (d-1)n + 1 - s_{\min}/2), (s_{\min}, 0)\}$ then we obtain the following lower bound,

$$G(\beta_1, \beta_2) \geq \max\{\log \Lambda_0 + 2(d-1)\beta_1, 4C/\pi + (d-1)\beta_2, 0\} \tag{4.22}$$

where Λ_0 is the growth constant for strongly embeddable trees and C is Catalan's constant. $4C/\pi \approx 1.166\dots$

In the next section we investigate numerically the free energy and phase behaviour of the solvent models for weakly and strongly embeddable animals and make comparisons to the bounds derived above.

5. Solvent models

In section 3 we discussed how the contact model and the solvent model for weakly embeddable animals were special cases of the two-variable model. In Madras *et al* (1990), the contact model was investigated and numerical estimates and bounds for the free energy were given. The results presented there correspond to the case $\beta_1 = 0$ in the two-variable model. Corresponding results for the solvent model have not been presented. Since the collapse transition can be driven by changing the solvent quality and, since the results in section 2 of this paper predict the location of the phase transition for the solvent model, it is an important model to investigate numerically. In this section we present numerical estimates of the free energy and heat capacity for this model and compare the estimates to the properties and bounds derived in sections 2 and 4, respectively. In addition, we look at numerical estimates for the solvent model for strongly embeddable lattice animals.

Let $q_n(s)$ be the number of lattice animals with n vertices and s solvent contacts, so that $q_n(s) = \sum_k a_n(s, k)$. We define the corresponding partition function

$$Q_n(\beta) = \sum_s q_n(s)e^{\beta s} \tag{5.1}$$

and the existence of the limit

$$\mathcal{F}(\beta) = \lim_{n \rightarrow \infty} n^{-1} \log Q_n(\beta) \tag{5.2}$$

follows from equation (2.6). Since $\mathcal{F}(\beta) = G(\beta, 0)$, the results of section 2 imply that $\mathcal{F}(\beta)$ is monotonic, convex and continuous, for $\beta < \infty$.

Since $p_c = 0.5$ for $d = 2$ and $p_c \approx 0.247$ (Essam 1972) for $d = 3$, the bounds derived in section 4 imply for $\beta < -\log \sqrt{2}$

$$\mathcal{F}(\beta) \geq \frac{4C}{\pi} \tag{5.3}$$

while for $-\log \sqrt{2} \leq \beta \leq 0$

$$\mathcal{F}(\beta) \geq \max\{d \log 2, \log \lambda + 2(d-1)\beta\} \tag{5.4}$$

where λ is the growth constant for weakly embeddable animals. For $\beta \geq 0$

$$\mathcal{F}(\beta) \geq \max\{\log \Lambda_0 + 2(d-1)\beta, \log \lambda\}. \tag{5.5}$$

The upper bound for $\beta \leq -\log \sqrt{2}$ is

$$\mathcal{F}(\beta) \leq d \log 2. \tag{5.6}$$

If λ_0 is the growth constant for weakly embeddable trees then for $[\log \lambda_0 + (d - 1) \log 2 - \log \lambda]/2(d - 1) > \beta > -\log \sqrt{2}$

$$\mathcal{F}(\beta) \leq \max\{\log \lambda, \log \lambda + 2(d - 1)\beta\} \tag{5.7}$$

and for $[\log \lambda_0 + (d - 1) \log 2 - \log \lambda]/2(d - 1) < \beta$

$$\mathcal{F}(\beta) \leq \max\{\log \lambda_0 + (d - 1) \log 2, \log \lambda_0 + 2(d - 1)\beta\}. \tag{5.8}$$

We have estimated the limiting free energy from exact enumeration data given in Madras *et al* (1990) with additional data due to Martin and Sykes (1992). The data include n values up to $n = 21$ for the square lattice and $n = 19$ for the simple cubic lattice. The limiting free energy estimates for weakly embeddable animals are shown in figure 2 for the square lattice and in figure 3 for the simple cubic lattice, together with the bounds summarized in equations (5.3) to (5.8). From these figures it is clear that the series analysis results are well converged in the expanded region and that the lower bound $\log \Lambda_0 + 2(d - 1)\beta$ is approached rapidly as β increases. In the compact regime the series results become progressively worse as β becomes more negative and the estimates are unreliable for $\beta \leq -1$ when $d = 2$ and for $\beta \leq -0.5$ when $d = 3$. This is undoubtedly connected with the highly compact nature of the dominating clusters in the compact regime but, since the estimates are below the lower bound, they indicate that the bound (5.3) will be good for large negative β .

From the percolation argument given in section 2 we know that $\mathcal{F}(-\log \sqrt{2}) = d \log 2$ and we have confirmed that the series data agree with this result. For the square lattice, we have also examined the way in which the limit is approached at this value of β by estimating the exponent θ' in

$$Z_n(-\log \sqrt{2}, 0) \sim n^{-\theta'} 4^n \tag{5.9}$$

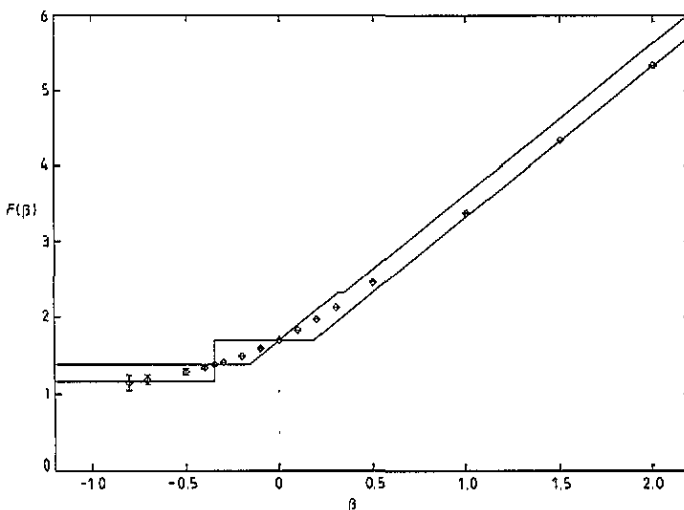


Figure 2. The β dependence of the limiting free energy for the solvent model for animals weakly embeddable in the square lattice.

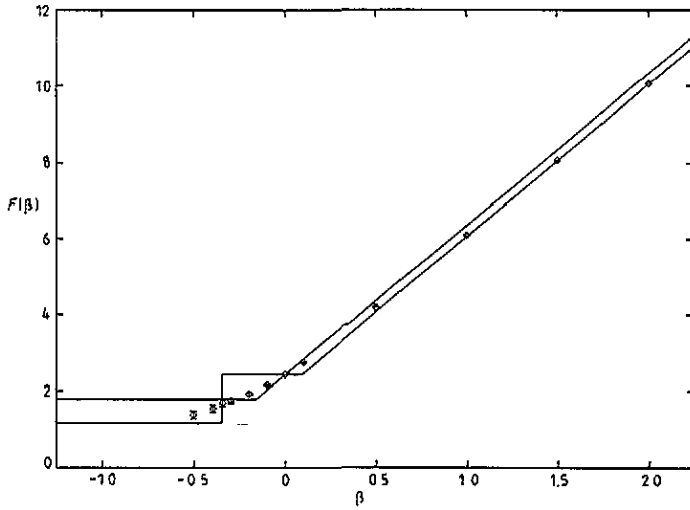


Figure 3. The β dependence of the limiting free energy for the solvent model for animals weakly embeddable in the simple cubic lattice.

by standard ratio methods. In figure 4 we show the n -dependence of the ratio estimates

$$\theta'_n = \frac{n}{2} \left(1 - \frac{Z_n}{4^2 Z_{n-2}} \right). \tag{5.10}$$

We estimate $\theta' = 2.06 \pm 0.01$ in excellent agreement with equation (2.17).

Also for the square lattice version of this model we have argued that the free energy is singular at $\beta = -\log \sqrt{2}$ (Flesia et al 1992b) and that larger values of β correspond to an expanded regime. (In fact we know that the point $(-\log \sqrt{2}, 0)$ is a singular point of $G(\beta_1, \beta_2)$ when approached along the curve

$$\beta_2 = \beta_1 + \log \left(\frac{e^{\beta_1}}{2} + \frac{\sqrt{e^{2\beta_1} + 4}}{2} \right) \tag{5.11}$$

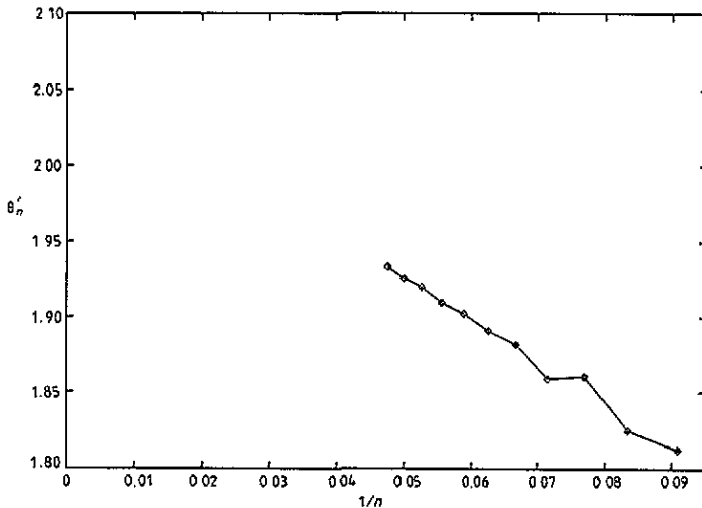


Figure 4. Ratio estimates of the exponent θ' for the square lattice.

but we have not proved that it is a singular point when approached along the β_1 axis.) To check this we have calculated the values of the heat capacities

$$C_n(\beta) = n^{-1} \frac{d^2 \log Z_n(\beta)}{d\beta^2} \tag{5.12}$$

as a function of β and n . The peak positions change as n increases, but approach a limiting value consistent with $-\log \sqrt{2}$. We fitted successive triples of points, $\beta_{\max}(n)$, to the form $\beta_c + An^{-0.6} - Bn^{-1}$ for $n = 5, \dots, 21$. The first correction term is the finite size scaling correction involving the crossover exponent ϕ which we take to have the value 0.6, while the second correction term is the first order analytic correction. (Although the value of ϕ is not known accurately for this model, changes in the second decimal place will have only a small effect on the fitting reported here.) For example, fitting the last three n values to this form, we obtain that $\beta_c \approx -0.3475$, $A \approx 3.6544$, $B \approx 5.4657$ and, using the sequence of values of β_c obtained in this way, we estimate $\beta_c = -0.35 \pm 0.05$. This is strong evidence that the transition occurs *exactly* at $\beta = -\log \sqrt{2} = -0.34657 \dots$

We can also look at the corresponding model for strongly embeddable animals. The limiting free energy for this model, $\hat{F}(\beta)$, was defined in equation (4.3). Equation (4.6) is an inequality relating $G(\beta_1, \beta_2)$ to $\hat{F}(\beta)$ and hence improved information about $\hat{F}(\beta)$ will lead to improved information about $G(\beta_1, \beta_2)$.

New bounds for $\hat{F}(\beta)$ were obtained in Flesia *et al* (1993) based on site percolation arguments. These lead to the following upper bounds for $\hat{F}(\beta)$. For $\beta \leq 0$

$$\hat{F}(\beta) \leq \min\{-\log(1 - e^\beta), \log \Lambda\} \tag{5.13}$$

where Λ is the growth constant for strongly embeddable animals, and for $\beta > 0$

$$\hat{F}(\beta) \leq \log \Lambda + 2(d - 1)\beta. \tag{5.14}$$

Given \hat{p}_c , the critical probability for site percolation, we obtain the following lower bounds, for $\beta < \frac{1}{2d} \log(1 - \hat{p}_c)$

$$\hat{F}(\beta) \geq \max\{-\log(1 - e^{2d\beta}), \log \Lambda + 2(d - 1)\beta\} \tag{5.15}$$

for $0 \geq \beta > \frac{1}{2d} \log(1 - \hat{p}_c)$

$$\hat{F}(\beta) \geq \log \Lambda + 2(d - 1)\beta \tag{5.16}$$

and for $\beta > 0$

$$\hat{F}(\beta) \geq \max\{\log \Lambda, \log \Lambda_0 + 2(d - 1)\beta\}. \tag{5.17}$$

As in the weakly embeddable version we estimate the limiting free energy from exact enumeration data. The estimates are shown in figure 5 for the square lattice and figure 6 for the simple cubic lattice, together with the bounds summarized above. It is again clear that the series analysis results are well converged in the expanded region and that the lower bound $\log \Lambda_0 + 2(d - 1)\beta$ is approached rapidly as β increases. In the compact regime the series results become progressively worse as β becomes more negative and the estimates are unreliable for $\beta \leq -1$ when $d = 2$ and for $\beta \leq -0.5$ when $d = 3$. For the square lattice, the model can be mapped into the model studied (using transfer matrix methods) by Derrida and Herrmann (1983) and their work predicts a transition at $\hat{\beta}_c \approx -0.935$. The free energy estimates imply that $\hat{F}(-0.935) > 0$ and in particular we estimate that $\hat{F}(-0.94) = 0.035 \pm 0.02$. This is consistent with the lower bound (5.13) and is further evidence that the critical behaviour of this lattice animal model is different from that of the vesicle model (see Flesia *et al* (1993)).

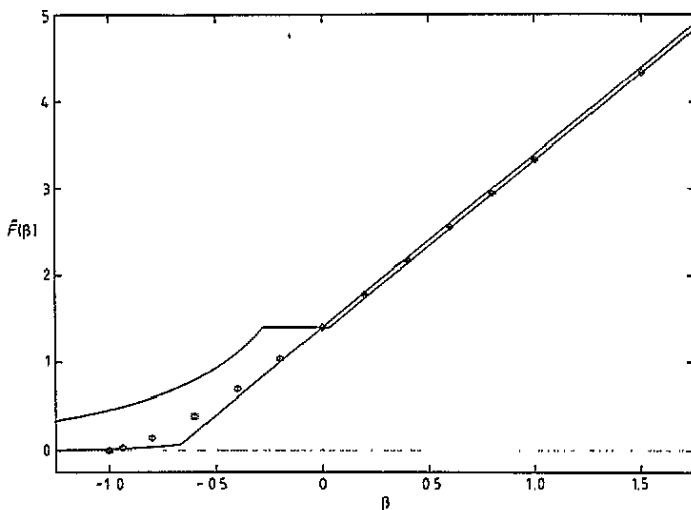


Figure 5. The β dependence of the limiting free energy for the solvent model for animals strongly embeddable in the square lattice.

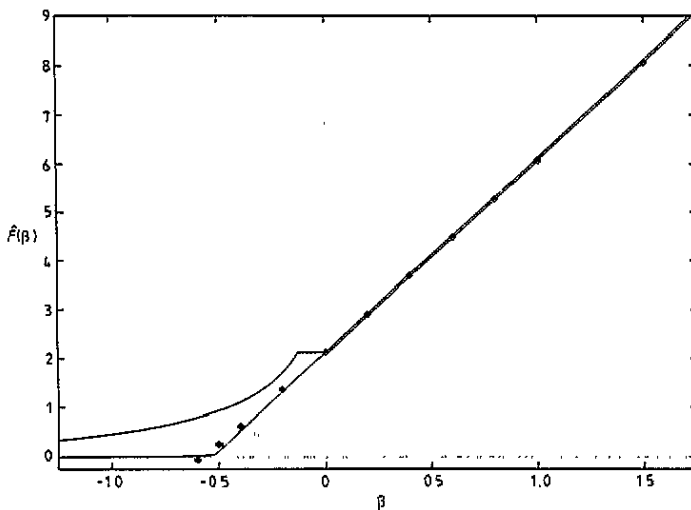


Figure 6. The β dependence of the limiting free energy for the solvent model for animals strongly embeddable in the simple cubic lattice.

The new bounds (5.15) and (5.13) provide some useful information regarding the two-variable model limiting free energy $G(\beta_1, \beta_2)$. In particular, equations (5.15) and (5.13) imply that

$$\lim_{\beta \rightarrow -\infty} \hat{F}(\beta) = 0 \tag{5.18}$$

while $\hat{F}(\beta) > 0$ for all $\beta > -\infty$. From equation (4.6) and the continuity of \hat{F}

$$\lim_{\beta_2 \rightarrow -\infty} G(\beta_1, \beta_2) = \hat{F}(\beta_1). \tag{5.19}$$

This combined with the fact that $\hat{F}(\beta_1) > 0$ for finite β_1 , rules out the possibility (left

open by equation (4.16)) that $G(\beta_1, \beta_2) = d \log(1 + e^{\beta_2})$ for $\beta_1 \geq \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$. However, we still have not rigorously ruled out the possibility (left open in equation (4.15)) that $G(\beta_1, \beta_2) = d \log(1 + e^{\beta_2})$ for $\beta_1 \leq \beta_2 - \frac{1}{2} \log(1 + e^{\beta_2})$ and $\beta_2 < \log[(1 - p_c)/p_c]$. However, the free energy estimates shown in figures 2 and 3 provide strong evidence that this is not possible.

6. The vesicle model

Vanderzande (1993) and Stella *et al* (1992) have suggested that the transition in animals might be connected with the collapse in vesicles. Their proposal rests on the mapping between a lattice and its dual, in which each vertex is replaced by its dual d -cell. For the square lattice every vertex is replaced by its dual two-cell, which in this case is an elementary square (or plaquette) in the (self-dual) square lattice. An animal with n vertices maps into an object which is composed of n plaquettes and therefore has area n . If this new object is topologically a disc, then the animal has been mapped into a vesicle (a polygon and the area which it encloses) with area n . Since each solvent contact in the original animal crosses an edge in the dual lattice which is on the perimeter of the vesicle, the vesicle has perimeter s . Of course, not every animal is dual to a disc. In particular, weakly embeddable animals with contacts cannot be dual to a disc, so we are restricted to strongly embeddable animals. Furthermore, a strongly embeddable animal which contains ‘holes’, or other structures leading to topological singularities in the dual surface, is not dual to a disc. These are severe restrictions and imply that animals dual to a disc are exponentially rare in the set of strongly embeddable animals.

The behaviour of vesicles is now quite well understood (Fisher *et al* 1991, Banavar *et al* 1991). In two dimensions, if $v_s(n)$ is the number of vesicles per lattice site with s perimeter edges, enclosing area n , we can write the generating function

$$\hat{A}_n(\beta) = \sum_s v_s(n) e^{\beta s} \tag{6.1}$$

where we note that e^β corresponds to the fugacity x in the notation of Fisher *et al* (1991). It follows from their arguments that

$$\mathcal{A}(\beta) = \lim_{n \rightarrow \infty} n^{-1} \log \hat{A}_n(\beta) \tag{6.2}$$

is monotonic non-decreasing, continuous, log-convex and almost everywhere differentiable. Moreover, there exists a $\beta_0 < 0$ such that $\mathcal{A}(\beta)$ is zero for $\beta < \beta_0$ and positive for $\beta > \beta_0$. Translating into a grand-canonical ensemble, to make the connection with the work of Vanderzande more transparent, we define

$$\mathcal{G}(e^\beta, y) = \sum_n A_n(\beta) y^n = \sum_{s,n} v_s(n) e^{\beta s} y^n \tag{6.3}$$

and use (6.2) to obtain

$$\mathcal{G}(e^\beta, y) = \sum_n e^{\mathcal{A}(\beta)n + o(n)} y^n \tag{6.4}$$

which converges if

$$y < e^{-\mathcal{A}(\beta)}. \tag{6.5}$$

This argument gives the form of the phase diagram shown in figure 2 of Vanderzande (1993) where our e^β corresponds to Vanderzande’s K and our y corresponds to Vanderzande’s p . The ‘phase boundary’ in that figure is just the boundary of convergence of \mathcal{G} , and this

boundary contains a singular point at $\beta = -\kappa$, $y = 1$, where (in two dimensions) κ is the connective constant of self-avoiding polygons on the square lattice.

Flesia et al (1993) have shown that for the solvent model for strongly embeddable animals the situation is somewhat different. Writing the grand-canonical partition function as

$$\hat{G} = \sum_{n,s} a_n(s, 0) e^{\beta s} y^n \quad (6.6)$$

\hat{G} converges if

$$y < e^{-\hat{F}(\beta)}. \quad (6.7)$$

The 'phase boundary' has a singular point corresponding to the collapse transition, occurring at $\beta = \beta_c \approx -0.935$ and $y = y_c < 1$. Since \hat{F} is never zero (see equation (5.15)), there is no vertical line in the phase diagram, corresponding to figure 2 of Vanderzande, for this model, and the 'phase boundary' approaches the y -axis smoothly at $y = 1$, in contrast to the vertical segment in the vesicle model. Flesia et al (1993) argue that this difference is due to the additional solvent perimeter associated with 'holes' in the object dual to the animal, and we now show this more explicitly. In particular, we show that for the solvent model for strongly embeddable animals the average number of solvent contacts, $\langle s \rangle \sim n$, provided $\beta > -\infty$. In contrast, in the solvent model for strongly embeddable animals dual to a disc (equivalent to the vesicle model) the average number of solvent contacts (perimeter edges for vesicles), $\langle s \rangle$, is $o(n)$ for $-\infty < \beta < x_0$. For the solvent model

$$\frac{\langle s \rangle}{n} = n^{-1} \frac{d \log A_n(\beta)}{d\beta} \quad (6.8)$$

and when we take the limit $n \rightarrow \infty$ we can interchange the order of the limit and derivative (almost everywhere) since the $A_n(\beta)$ are convex, increasing functions of β . Hence

$$\lim_{n \rightarrow \infty} \frac{\langle s \rangle}{n} = \hat{F}'(\beta). \quad (6.9)$$

Since $\hat{F}(\beta)$ is strictly increasing then equation (6.9) implies that $\langle s \rangle \sim n$. A similar argument for the vesicle model shows that

$$\lim_{n \rightarrow \infty} \frac{\langle s \rangle}{n} = \mathcal{A}'(\beta) \quad (6.10)$$

and this equation, together with the fact that $\mathcal{A}'(\beta) = 0$ for $\beta < x_0$, implies that $\langle s \rangle = o(n)$ for $\beta < x_0$. Therefore there is a fundamental difference in the thermodynamics of these two models. In the notation of Brak et al (1993), the vesicle model is *asymmetric* while the solvent model for strongly embeddable animals is *symmetric*. This means that the heat capacity exponent α cannot be defined for the vesicle model when the transition is approached from the small β direction.

Perhaps this is even clearer if we examine the situation in the constant s ensemble. For the vesicle problem we know that the limiting free energy in this ensemble at $y = 1$ is equal to κ . For strongly embeddable animals this limiting free energy is infinite at $y = 1$, as can be seen from the above arguments (i.e. by switching ensembles) or by the following. Equation (6.6) can be rewritten as

$$\hat{G} = \sum_s \left(\sum_n a_n(s, 0) y^n \right) e^{\beta s} \equiv \sum_s H_s(y) e^{\beta s}. \quad (6.11)$$

We next obtain a lower bound on $H_s(y)$. To obtain a lower bound, consider the set of strongly embeddable animals formed in the following way. Start with a building block

which is a 3×3 square of 9 vertices and build up a bigger square animal from l rows of l intersecting building blocks. The bigger animal is made up of l^2 building blocks ($(2l + 1)^2$ vertices, $8l + 4$ solvent contacts) and in the centre of each block is a vertex. Remove any l of the centre vertices. This yields an animal with $n = 4l^2 + 3l + 1$ vertices and $s = 12l + 4$ solvent contacts. There are $\binom{l^2}{l}$ distinct animals of this kind. Hence

$$H_{12l+4}(y) \geq \binom{l^2}{l} y^{4l^2+3l+1}. \tag{6.12}$$

An easy calculation then shows that $n^{-1} \log H_n(1)$ goes to infinity at least as rapidly as $\log n$. Therefore the limiting free energy in this ensemble at $y = 1$ is infinite.

We summarize the results of this section in figure 7 where we compare the behaviour of the vesicle problem and the strongly embeddable animal problem in the grand canonical ensemble.

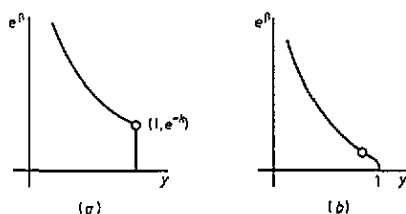


Figure 7. Sketch of the boundaries of convergence in the grand canonical ensemble for (a) the vesicle model and (b) the solvent model for strongly embeddable animals.

7. Discussion

We have examined the properties of a two-variable model for branched polymers in dilute solution. In particular we have explored the general features of the free energy, derived bounds on its behaviour, and discussed connections between this model and several one variable models which have appeared in the literature. In addition we have derived bounds on the free energy for two solvent models and estimated the limiting free energies numerically using exact enumeration data. Finally we have discussed a vesicle model which was introduced by Vanderzande (1993) and pointed out significant differences between the behaviour of this model and one of the solvent models analysed in section 5.

We have focussed on the behaviour of the free energy of these models but this gives rather little information about phase transitions. By a connection to percolation theory we showed that the free energy was singular at at least one point in the two-variable model and we have argued that this allows us to predict the exact location of the collapse transition in a solvent model. Further investigation at or near the phase transition, using Monte Carlo methods, would give useful additional information.

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