Lattice animal contact models of a collapsing branched polymer

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Abstract. We consider two lattice animal models for the collapse of dilute branched polymers in a good solvent. In both cases, the collapse is driven by a near-neighbour contact fugacity, the two models differing in the way molecular weights are assessed, either by the site content or the bond content of the animal. We describe some rigorous results, including bounds, for the temperature dependence of their reduced limiting free energies on a d-dimensional hypercubic lattice and compare these results with numerical estimates derived from exact enumeration data. From the specific heat, we estimate the collapse temperature of both models on a variety of lattices. In addition, we estimate the cross-over exponent ϕ and find that for both models $\phi = 0.60 \pm 0.03$ ($d = 2$) and $\phi = 0.82 \pm 0.02$ ($d = 3$).

1. Introduction

Recently, there has been considerable interest in modelling the collapse of randomly branched polymers in dilute solution, using either lattice animals (Derrida and Herrmann 1983, Dickman and Schieve 1984, Lam 1987, 1988, Chang and Shapir 1988, Madras *et al* 1988, 1990, Gaunt and Flesia 1990, Gaunt 1991), lattice trees (Madras *et al* 1990, Gaunt and Flesia 1991) or lattice animals with a fixed cyclomatic index (c) i.e. c-animals (Flesia 1992, Flesia *et al* 1992). As the solvent quality decreases, or, alternatively, the temperature decreases, the branched polymers become more compact and a tricritical collapse transition is expected to occur. The existence of a collapse transition for branched polymers has been proven (Dhar 1987) only for a 2D directed animal model.

Most work has focused on two basic types of model. In one of these, the collapse is driven by something equivalent to a cycle fugacity (Derrida and Herrmann 1983, Dickman and Schieve 1984, Lam 1987, 1988, Chang and Shapir 1988, Madras *et al* 1988, 1990, Gaunt and Flesia 1990). In the other sort of model, the driving force is a near-neighbour contact fugacity (Madras *et al* 1990, Gaunt and Flesia 1990, 1991, Flesia 1992, Flesia *et al* 1992). (Two vertices form a contact if they are non-bonded near neighbours.) Contact models have also been used to study the internal transition that occurs in linear polymers (see e.g. the references cited by Derrida and Herrmann 1983 and Madras *et al* 1990).

Very recently, a solvent perimeter model has been introduced (Flesia 1992, Flesia *et al* 1992) in which the collapse is driven explicitly by solvent quality, i.e. by a repulsive interaction between each vertex of the animal and nearest-neighbour unoccupied sites of the lattice. For the case of c-animals, they showed that there is an exact mapping between the thermodynamics of this model and the thermodynamics of the contact

model, and that the limiting free energy is independent of c in both models. For the contact model, this implies that, if a collapse transition exists at $\beta = \beta_0$ (where e^β is the contact fugacity) for trees ($c = 0$), then a collapse transition occurs at β_0 for all values of c. The critical point of the solvent perimeter model is then $-\beta_0/2$, independent of c and, moreover, critical exponents such as α are the same for both models, independent of c.

The contact model for lattice trees has been studied by Gaunt and Flesia (1991). Here we present corresponding results for lattice animals. Clearly, the animals must be weakly embedded in the underlying lattice (i.e. they must be subgraphs) since for strongly embedded clusters (i.e. section graphs) the number of contacts (k) is zero by definition. For lattice animals, their size may be classified either by their site content or by their bond content. We have referred to these cases as the λ- and λ'-models, respectively (Gaunt and Flesia 1990). For lattice trees, this distinction was unnecessary since the numbers of sites and of bonds in a tree are trivially related by Euler's relation.

Let us write $a_n(k)$ and $a'_n(k)$ for the number of weakly embedded animals with n sites and k contacts, and n bonds and k contacts, respectively. The partition function of the λ-model is then

$$Z_n(\beta; \lambda) = \sum_k a_n(k) \, e^{\beta k}. \tag{1.1}$$

We note that $\beta > 0$ corresponds to attractive interactions and $\beta < 0$ to repulsive interactions. We define the corresponding reduced free energy by

$$F_n(\beta; \lambda) = n^{-1} \log Z_n(\beta; \lambda) \tag{1.2}$$

and the reduced limiting free energy by

$$F(\beta; \lambda) = \lim_{n \to \infty} F_n(\beta; \lambda). \tag{1.3}$$

Analogous expressions for the λ'-model are obtained by replacing a by a' in (1.1).

In section 2, we summarize what is known rigorously (Madras *et al* 1990) about $F(\beta; \lambda)$ and $F(\beta; \lambda')$ for a d-dimensional simple hypercubic lattice. In section 3, the rigorous results are compared with numerical estimates for the square and simple cubic lattices. We study the specific heat numerically in section 4 and estimate the transition point β_c and the cross-over exponent ϕ for the λ- and λ'-models in two and three dimensions. Finally, in section 5, we discuss our results for the cross-over exponent and compare them with corresponding results for lattice trees (Gaunt and Flesia 1991) and for a cycle model (Derrida and Herrmann 1983, Lam 1988, Chang and Shapir 1988) that has been widely used for studying the collapse transition in branched polymers.

2. Free energy: rigorous results

For a d-dimensional simple hypercubic lattice, Madras *et al* (1990) have proved a number of rigorous results for the reduced limiting free energy, which we summarize for use later.

Firstly, the limit defined in (1.3) for the λ-model, and the corresponding limit for the λ'-model, exist for $-\infty \le \beta < \infty$. Furthermore, $F(\beta; \lambda)$ and $F(\beta; \lambda')$ are monotone, non-decreasing, convex and continuous for $-\infty < \beta < \infty$. If Λ_s and Λ_b are the growth constants for strongly embedded animals with site and bond counting, respectively,

and λ_s and λ_b are the corresponding growth constants for weakly embedded animals, then

$$F(-\infty; \lambda) = \log \Lambda_s \qquad F(0; \lambda) = \log \lambda_s \tag{2.1}$$

and

$$F(-\infty; \lambda') = \log \Lambda_b \qquad F(0; \lambda') = \log \lambda_b. \tag{2.2}$$

In addition, it can be proved that

$$\lim_{\beta \to -\infty} F(\beta; \lambda) = \log \Lambda_s \tag{2.3}$$

and

$$\lim_{\beta \to -\infty} F(\beta; \lambda') = \log \Lambda_b. \tag{2.4}$$

Some intermediate results used to establish the behaviour in the $\beta \to -\infty$ limit also give rise to upper bounds which are useful for $\beta < 0$, namely

$$F(\beta; \lambda) \leqslant \min\{\log \lambda_s, \log \Lambda_s + d \log(1 + e^\beta)\} \qquad \beta < 0 \tag{2.5}$$

and

$$F(\beta; \lambda') \leqslant \min\{\log \lambda_b, \log \Lambda_b + d \log(1 + \Lambda_b e^\beta)\} \qquad \beta < 0. \tag{2.6}$$

For both models, F is bounded for $\beta > 0$ by

$$\max\{F(0), (d-1)\beta\} \leqslant F(\beta) \leqslant F(0) + (d-1)\beta \qquad \beta > 0. \tag{2.7}$$

Dividing (2.7) by β and letting $\beta \to \infty$ gives

$$\lim_{\beta \to \infty} F(\beta)/\beta = d - 1. \tag{2.8}$$

Moreover, there is an asymptotic line

$$L(\beta) = (d-1)\beta + S \tag{2.9}$$

such that

$$\lim_{\beta \to \infty} \{F(\beta) - L(\beta)\} = 0.$$

Physically, S is interpreted as the reduced limiting entropy of the compact phase. For both models, S is strictly positive and is bounded below by

$$S \geqslant \pi^{-d} \int_0^\pi \cdots \int_0^\pi \log\left(2d - 2 \sum_{i=1}^d \cos \alpha_i\right) d\alpha_1 \ldots d\alpha_d. \tag{2.10}$$

For the square lattice, this gives $4C/\pi = 1.166\ldots$, where C is Catalan's constant, and for the simple cubic lattice, $1.673\ldots$ (Gaunt and Flesia 1991). Combining the above information gives improved bounds on $F(\beta)$ for $\beta > 0$ of

$$\max\{F(0), \beta + 1.166\ldots\} \leqslant F(\beta) \leqslant F(0) + \beta \qquad d = 2 \tag{2.11}$$

and

$$\max\{F(0), 2\beta + 1.673\ldots\} \leqslant F(\beta) \leqslant F(0) + 2\beta \qquad d = 3. \tag{2.12}$$

We note, for use in section 3, the numerical estimates (Guttmann and Gaunt 1978, Gaunt and Ruskin 1978, Gaunt and Flesia 1990, Gaunt 1991 and unpublished)

$$\log \lambda_s = 1.704 \pm 0.002 \qquad \log \Lambda_s = 1.4019 \pm 0.0005$$
$$\log \lambda_b = 1.651 \pm 0.002 \qquad \log \Lambda_b = 1.355 \pm 0.002 \tag{2.13}$$

for the square lattice, and

$$\log \lambda_s = 2.434 \pm 0.009 \qquad \log \Lambda_s = 2.121 \pm 0.003$$
$$\log \lambda_b = 2.364 \pm 0.005 \qquad \log \Lambda_b = 2.0677 \pm 0.0005 \tag{2.14}$$

for the simple cubic lattice.

3. Free energy: numerical results

In this section, we report numerical estimates of $F(\beta; \lambda)$ and $F(\beta; \lambda')$ for the square and simple cubic lattices, and compare these estimates with the rigorous results described in section 2.

Our numerical estimates are based on new exact enumeration data (Madras et al 1990) with the number of sites $n \leqslant 19$ on the square lattice and $n \leqslant 17$ on the simple cubic lattice. We begin by using these data to calculate exactly the reduced free energies $F_n(\beta; \lambda)$ and $F_n(\beta; \lambda')$ (see e.g. (1.2)), for values of β in the interval $-4 \leqslant \beta \leqslant 6$. We do not give the plots since they are very similar to those for the t-model (lattice trees); see e.g. figure 1 of Gaunt and Flesia (1991). The curves lie mostly outside the region delineated by the rigorous bounds given in section 2. The reduced limiting free energies $F(\beta; \lambda)$ and $F(\beta; \lambda')$, defined by (1.3) for example, are then estimated numerically using ratio and Padé approximant methods (Gaunt and Guttmann 1974, Gaunt and Flesia 1990, Madras et al 1990). Our best estimates of $F(\beta; \lambda)$ and $F(\beta; \lambda')$ for the square and simple cubic lattices for $-4.0 \leqslant \beta \leqslant 1.5$ and $-4.0 \leqslant \beta \leqslant 1.0$, respectively, are given in table 1. $F(\beta; \lambda')$ is plotted in figures 1 and 2 for the square and simple cubic lattices, respectively, together with the rigorous bounds given in section 2. Corresponding plots for $F(\beta; \lambda)$ have been given in figure 3 of Madras et al (1990) for the square lattice, and in figure 1 of Gaunt (1991) for the simple cubic lattice.

For all $\beta \leqslant 0$, as well as for small positive values of β, the numerical estimates are very precise. For larger values of β, the uncertainties increase rapidly in size. For all values of β, our estimates satisfy the rigorous bounds. For large $\beta > 0$, our results suggest that for the λ- and λ'-models on the square and simple cubic lattices, the lower bound is (or is very nearly) the exact asymptote. This implies that the reduced limiting entropy (S) of the compact phase, defined in (2.9), is given by the expression on the right-hand side of (2.10). We recall that we made the same conjecture for the t-model (lattice trees) on the square and simple cubic lattices.

Finally, as expected, $F(\beta; \lambda)$ and $F(\beta; \lambda')$ are rather smooth and we have been unable to detect any sign of the collapse transition which is expected to occur for some value of $\beta = \beta_c > 0$.

4. Specific heat

Rather than attempt numerical differentiation of $F(\beta; \lambda)$ and $F(\beta; \lambda')$ in order to estimate the specific heat, we follow the approach taken by other workers and differentiate $F_n(\beta; \lambda)$ and $F_n(\beta; \lambda')$ before taking the $n \to \infty$ limit. Accordingly, we define the

Table 1. Estimates of the reduced limiting free energies of the λ- and λ'-models on the square and simple cubic lattices.

|	Square		Simple cubic	
β	$F(\beta;\lambda)$	$F(\beta;\lambda')$	$F(\beta;\lambda)$	$F(\beta;\lambda')$
−4.0	1.403 ± 0.001	1.360 ± 0.002	2.1260 ± 0.0005	2.0720 ± 0.0005
−3.5	1.406 ± 0.002	1.363 ± 0.002	2.1289 ± 0.0005	2.0749 ± 0.0005
−3.0	1.417 ± 0.002	1.368 ± 0.002	2.1339 ± 0.0005	2.0798 ± 0.0005
−2.5	1.421 ± 0.002	1.378 ± 0.002	2.1423 ± 0.0005	2.0880 ± 0.0005
−2.0	1.442 ± 0.002	1.393 ± 0.002	2.1565 ± 0.0005	2.1017 ± 0.0005
−1.5	1.462 ± 0.002	1.413 ± 0.001	2.1809 ± 0.0005	2.1248 ± 0.0005
−1.0	1.508 ± 0.002	1.455 ± 0.001	2.222 ± 0.002	2.164 ± 0.001
−0.5	1.581 ± 0.002	1.527 ± 0.001	2.293 ± 0.002	2.235 ± 0.002
0	1.704 ± 0.002	1.650 ± 0.001	2.434 ± 0.004	2.360 ± 0.003
0.1	1.737 ± 0.002	1.6838 ± 0.0004	2.481 ± 0.008	2.402 ± 0.003
0.2	1.774 ± 0.002	1.7217 ± 0.0002	2.534 ± 0.008	2.451 ± 0.004
0.3	1.815 ± 0.004	1.7635 ± 0.0015	2.603 ± 0.008	2.514 ± 0.004
0.4	1.860 ± 0.006	1.8095 ± 0.0015	2.695 ± 0.014	2.599 ± 0.005
0.5	1.918 ± 0.006	1.8600 ± 0.0020	2.83 ± 0.06	2.69 ± 0.01
0.6	1.967 ± 0.008	1.9135 ± 0.0020	2.94 ± 0.10	2.82 ± 0.03
0.7	2.024 ± 0.008	1.971 ± 0.007	3.10 ± 0.15	2.99 ± 0.05
0.8	2.08 ± 0.01	2.055 ± 0.02	3.25 ± 0.15	3.18 ± 0.15
0.9	2.14 ± 0.01	2.13 ± 0.04	3.40 ± 0.20	3.3 ± 0.20
1.0	2.20 ± 0.01	2.21 ± 0.05	3.55 ± 0.20	3.5 ± 0.25
1.1	2.28 ± 0.02	2.30 ± 0.05		
1.2	2.35 ± 0.03	2.39 ± 0.06		
1.3	2.42 ± 0.05	2.47 ± 0.07		
1.4	2.50 ± 0.07	2.57 ± 0.09		
1.5	2.55 ± 0.10	2.66 ± 0.10		
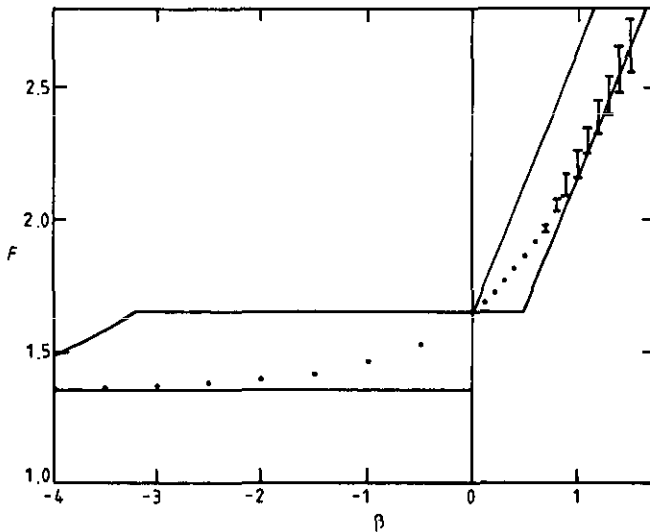
Figure 1. Numerical estimates of the reduced limiting free energy $F(\beta)$ for the λ'-model on the square lattice. Estimated errors are given unless smaller than the symbols. Upper and lower bounds are also included.
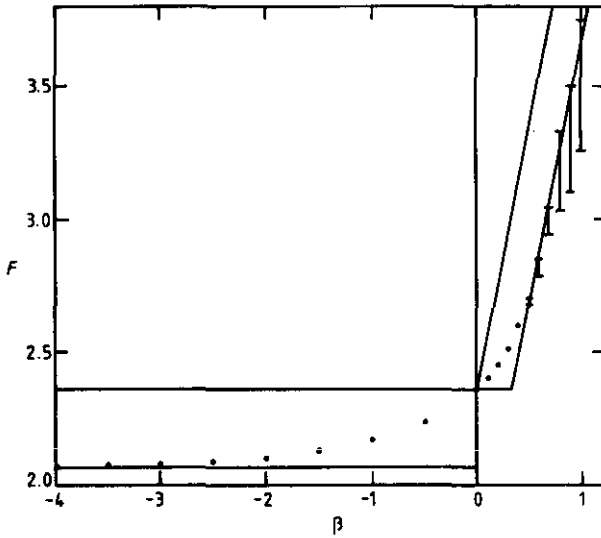
Figure 2. As figure 1 but on the simple cubic lattice.

specific heat through

$$C_n(\beta; \lambda) = (d^2/d\beta^2)F_n(\beta; \lambda) = (\langle k^2 \rangle - \langle k \rangle^2)/n \tag{4.1}$$

and a similar expression for $C_n(\beta; \lambda')$. For a given lattice, $C_n(\beta; \lambda)$ and $C_n(\beta; \lambda')$ have essentially the same shape as $C_n(\beta; t)$ for the t-model, viz. they all exhibit sharp peaks which increase smoothly in height as n increases, and have secondary features which are characteristic of the lattice. As an example, we plot in figure 3 $C_n(\beta; \lambda)$ for the simple cubic lattice. For certain values of n, the peak is higher and displaced to a larger value of β relative to the peaks for $(n-1)$ and $(n+1)$. For $n = 15$ (λ-model) and $n = 14$ (λ'-model) on the body-centred cubic lattice, there is a secondary peak, at
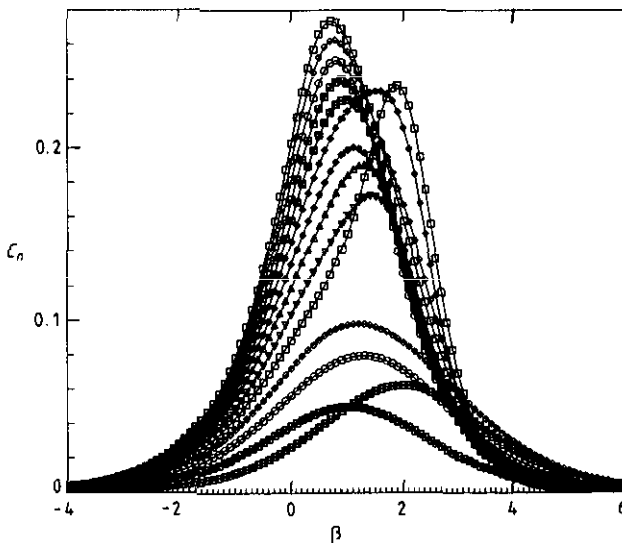

Figure 3. The specific heat $C_n(\beta)$ for the λ-model on the simple cubic lattice for $n = 4$–17.

a larger value of β than the principal peak. A very similar peak was observed in the t-model for $n = 15$ (see Gaunt and Flesia 1991, figure 7). For the square lattice, the curves have a rather small, but quite definite, 'shoulder' at large values of β (for the t-model, see Gaunt and Flesia 1991, figure 4). It has been suggested that all these low-temperature features are manifestations of roughening (Dickman and Schieve 1984, Lam 1987, Gaunt and Flesia 1990, 1991).

According to finite-size scaling theory, the height h_n of the principal maximum scales as

$$h_n \sim n^{\alpha\phi} \qquad n \to \infty \tag{4.2}$$

where ϕ is the cross-over exponent and α is the specific heat exponent. Assuming α and ϕ are related by the 'hyperscaling' relation

$$2 - \alpha = 1/\phi \tag{4.3}$$

(see e.g. Derrida and Herrmann 1983), gives

$$h_n \sim n^{2\phi-1} \qquad n \to \infty. \tag{4.4}$$

To estimate ϕ, we calculate

$$\phi_n = \frac{1}{2}\left[\frac{\log(h_n/h_{n-1})}{\log(n/n-1)} + 1\right] \tag{4.5}$$

which should approach ϕ as $n \to \infty$. In figure 4, we plot ϕ_n and their adjacent linear extrapolants against $1/n$ for the λ- and λ'-models on the square lattice. We estimate that for both models
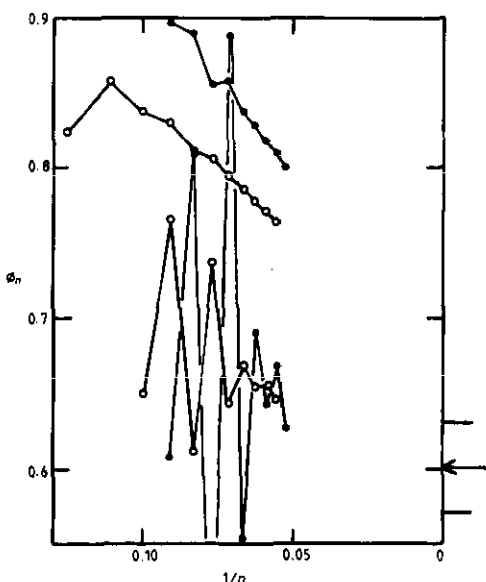
$$\phi = 0.60 \pm 0.03 \qquad d = 2. \tag{4.6}$$

Figure 4. ϕ_n (upper curves) and their extrapolants (lower curves) plotted against $1/n$ for the λ- and λ'-models ($\bullet$ and $\bigcirc$, respectively) on the square lattice. Our best estimate of ϕ is indicated on the right-hand axis.

Corresponding plots for the body-centred cubic lattice, together with less well converged results for the simple cubic and diamond lattices, are given in figures 5 and 6 for the λ- and λ'-models, respectively. In addition, the equivalent of figure 4 but for the body-centred cubic lattice has been plotted in figure 2 of Gaunt (1991). We conclude that for both models on all 3D lattices,

$$\phi = 0.82 \pm 0.02 \qquad d = 3. \tag{4.7}$$

According to finite size scaling theory, the values of β at which the specific heat curves have their principal maximum, namely $\beta_{\max}(n)$, should approach β_c like

$$\beta_{\max}(n) = \beta_c + An^{-\phi} - Bn^{-1} + \ldots \qquad n \to \infty \tag{4.8}$$

where A and B are constant amplitudes. In figure 7, $\beta_{\max}(n)$ is plotted against $n^{-\phi}$ for the λ- and λ'-models on several lattices using the central value of ϕ in (4.6) and (4.7). The curves for the λ- and λ'-models on a given lattice are quite similar to one another and to the corresponding curve for the t-model on the same lattice (see Gaunt and Flesia 1991, figure 8). In all cases, the curves become relatively smooth for large values of n and, in the case of the square lattice, pass through a minimum. We have tried to estimate β_c by solving (4.8) and have obtained the results presented in table 2. Estimates for the t-model (Gaunt and Flesia 1991) are given for comparison. For
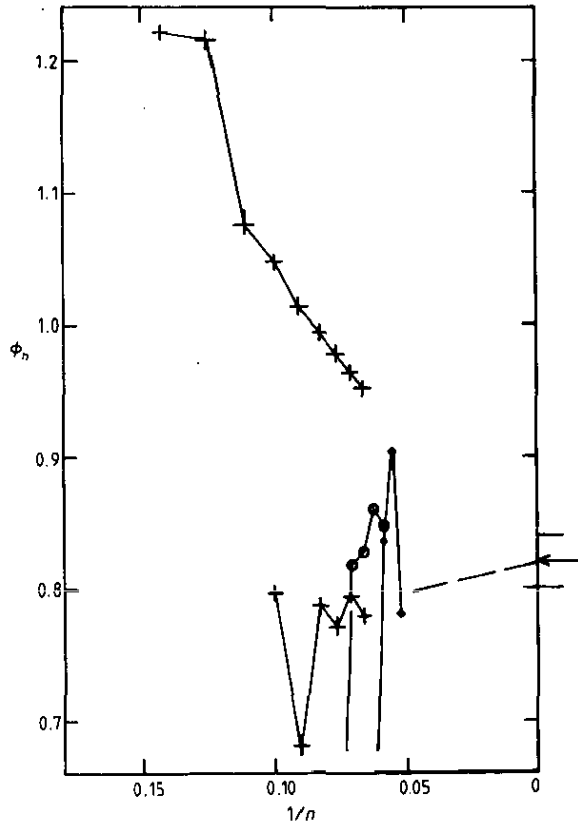

Figure 5. ϕ_n and their extrapolants plotted against $1/n$ for the λ-model on the body-centred cubic lattice (+), together with ϕ_n for the simple cubic (○) and diamond (◇) lattices. Our best estimate of ϕ is indicated on the right-hand axis.
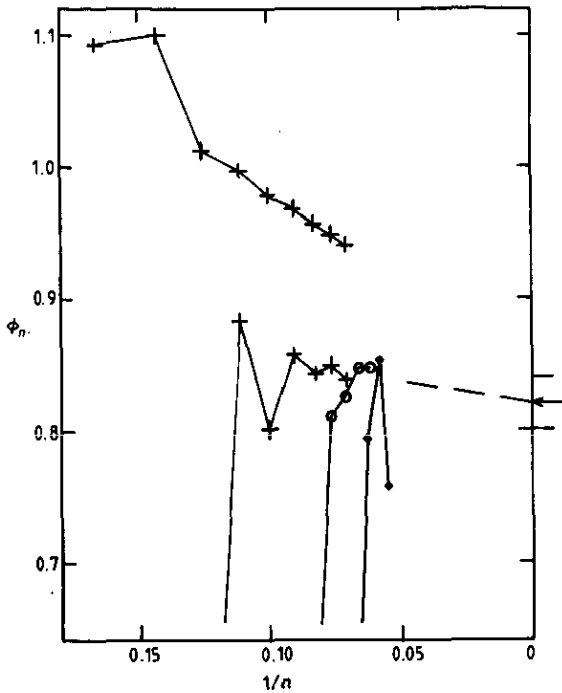
Figure 6. As figure 5 but for the λ'-model.

the diamond lattice, estimates are not possible since the estimators are too erratic to allow extrapolation.

For all three contact models, the central estimates suggest that a 2D system collapses at a lower temperature than a 3D system. The same is true for a cycle model of strongly embeddable lattice animals with site counting (Derrida and Herrmann 1983, Lam 1987, 1988). The coordination number of the embedding lattice is also important. For example, in three dimensions, we expect that a branched polymer on the body-centred cubic lattice will collapse sooner than one on the simple cubic lattice, because near neighbours are more abundant in the former case. The results in table 2 support this conclusion for all three models. Finally, we note that for a given lattice in either two or three dimensions, it appears that the λ-model collapses before the λ'-model, which in turn collapses before the t-model.

5. Summary and discussion

In this paper, we have investigated numerically the collapse transition that occurs in two lattice animal models of branched polymers, namely the λ- and λ'-models, in which the collapse is driven by a near-neighbour contact fugacity.

In section 2, we summarized some rigorous results (Madras *et al* 1990), including upper and lower bounds for the temperature dependence of the reduced limiting free energies on a d-dimensional hypercubic lattice. In section 3, we obtained numerical estimates of $F(\beta; \lambda)$ and $F(\beta; \lambda')$ for the square and simple cubic lattices (see table 1), which satisfy the rigorous bounds for all values of β and which suggest that the
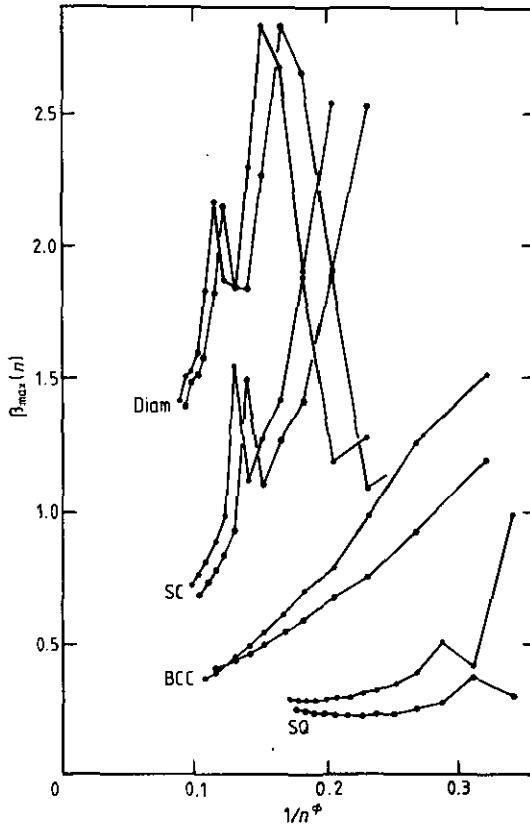
Figure 7. $\beta_{\max}(n)$ plotted against $1/n^{0.60}$ on the square lattice and against $1/n^{0.82}$ on the diamond, simple cubic and body-centred cubic lattices for the λ- and λ'-models (● and ○, respectively).

Table 2. Estimates of the collapse transition point β_c for contact models on the square (sq), simple cubic (sc) and body-centred cubic (bcc) lattices.

	λ	λ'	t
sq	0.38 ± 0.05	0.45 ± 0.1	0.5 ± 0.1
sc	0.3 ± 0.3	0.35 ± 0.3	0.35 ± 0.3
bcc	0.23 ± 0.01	0.32 ± 0.02	0.33 ± 0.1

lower bound for large $\beta > 0$ is the exact asymptote as $\beta \to \infty$. This implies that the reduced limiting entropy S of the compact phase is given by the right-hand side of (2.10). The same result appears to be valid (Gaunt and Flesia 1991) for the lattice tree version of these models (i.e. the t-model). In section 4, we have used the specific heat and finite size scaling to estimate the collapse transition point β_c and our results are summarized in table 2. In addition, we have estimated the cross-over exponent as $\phi = 0.60 \pm 0.03$ in two dimensions and $\phi = 0.82 \pm 0.02$ in three dimensions. The central values coincide with our best estimates for the t-model (Gaunt and Flesia 1991) and for a contact model of c-animals (Flesia *et al* 1992). It seems that all contact models, whether of lattice animals (λ, λ'), lattice trees (t) or c-animals, are in the same

universality class. This supports the suggestion, first made by Lubensky and Isaacson (1979), that cycles are relatively unimportant in determining the universality class of branched polymers.

These values of ϕ may be compared with corresponding estimates for a cycle (C-) model of lattice animals, strongly embeddable in the lattice with site counting. For this model, $\phi = 0.657 \pm 0.025$ in two dimensions (Derrida and Herrmann 1983), while in three dimensions, there are conflicting estimates of $\phi \approx 0.814$ (Lam 1988) and $\phi \approx 1$ (Chang and Shapir 1988). These results indicate that contact models and cycle models may be in different universality classes, but the evidence is not conclusive.

Acknowledgments

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