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Branched polymers: exact enumeration study of three-dimensional lattice animals classified by valence distribution

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Abstract. The partial generating function method is applied to the enumeration of lattice animals classified according to their valence distribution. This detailed information allows one to study the effects of the number and nature of branch points on the properties of branched polymers. Several series analysis techniques are applied to the data. Particular attention is given to the effects of correction-to-scaling terms.

1. Introduction

Lattice animals and related objects have recently been studied in some detail as models of branched polymers with excluded volume; of particular interest is the nature of the dependence of universality class (UC) on the degree and number of branch points. In this paper we address a number of these somewhat similar problems by applying the partial generating function method of Sykes (1986a) to the enumeration of three-dimensional site and bond animals classified by their valence distribution. In the terminology of Wilkinson (1986) these constitute *local* problems. The data thus produced are very detailed and one is able to regroup to consider the better known varieties of branched polymer (e.g. c animals, restricted valence animals; see below). A selection of the derived data are subsequently analysed and particular reference is made to the effects of correction-to-scaling terms.

Unrestricted (i.e. ordinary) lattice animals were apparently first studied in the context of randomly branched polymers by Lubensky and Isaacson (1979). One normally assumes that the number of unrestricted lattice animals, $A_n(q)$ (here n refers to the number of sites (bonds) in the site (bond) problem) has the asymptotic form

$$A_n(q) \sim n^{-\theta}\{\Lambda(q)\}^n \qquad (n \to \infty) \tag{1}$$

where $\Lambda(q)$ is the non-universal animal growth parameter and θ is a universal exponent. (The notation indicates that unrestricted animals are here treated as having a maximum valence restricted only by the lattice coordination number q.) There is convincing non-numerical evidence (Parisi and Sourlas 1981) that in three dimensions $\theta = 1.5$ exactly, which is in accord with numerous series estimates (Gaunt *et al* 1976, Sykes and Glen 1976, Sykes *et al* 1976, Gaunt and Ruskin 1978, Gaunt *et al* 1979, Whittington *et al* 1979, Gaunt 1980).

Domb (1976) has proposed an alternative to (1):

$$A_n(q) \sim n^{-\theta}\{\Lambda(q)\}^n \exp(-F/n^{t-1}) \tag{2}$$

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where F and t are additional parameters. This form has received some theoretical support (Lubensky and McKane 1981, Harris and Lubensky 1981) and appears to fit the data very well (Guttmann and Gaunt 1978, Guttmann 1982). In some sense (2) can be thought of as incorporating correction-to-scaling terms, which are normally assumed to be present (see, e.g., Margolina *et al* 1983).

For c animals, i.e. animals with precisely c cycles, Whittington *et al* (1983) give the equivalent of (1) as

$$A_{n,c} \sim n^{-(\theta_0 - c)} \Lambda_0^n \tag{3}$$

where θ_0 and Λ_0 are respectively the exponent and growth parameter for trees (i.e. 0 animals), and it is thought that $\theta_0 = \theta$ (Duarte and Ruskin 1981, Gaunt *et al* 1982, Ruskin and Duarte 1982, Whittington *et al* 1983).

Animals that are not allowed to contain any vertex with valence greater than some specified maximum, i.e. restricted valence animals, have been suggested as models of branched polymers with steric hindrance (Kertész *et al* 1982, Stauffer *et al* 1982). It is assumed that for $v \geqslant 3$

$$A_n(v) \sim n^{-\theta} \{\Lambda(v)\}^n \tag{4}$$

where v is the maximum allowed valence. When $v = q$ we simply have (1). Such animals embedded in the simple cubic (SC) lattice have been discussed by Gaunt *et al* (1980).

The topologies of sufficiently simple molecules are determined by their valence distribution. For the number, A_n^T, of lattice animals with some specified topology (T), Gaunt *et al* (1984a, b) assume

$$A_n^T \sim n^{\gamma_T - 1} \mu^n \tag{5}$$

where it may be proved that μ is the self-avoiding walk (SAW) or neighbour-avoiding walk (NAW) growth parameter for weak and strong embeddings, respectively. It has been conjectured (Gaunt *et al* 1984a, b) that $\gamma_T = \gamma + b - 1$ where γ is the corresponding exponent for SAW and b is the number of branches in the topology. The current best estimate of γ is the renormalisation group (RG) result $\gamma = 1.1615 \pm 0.0020$ (Le Guillou and Zinn-Justin 1980).

The plan of this paper is as follows: in § 2 details of the application of Sykes' partial generating function method to the enumeration of lattice animals classified by valence distribution are given. The same is done for bond problems in § 3. A selection of the new data is given in (13), (14) and the appendix. In § 4 the results of the series analysis are given. Finally, in § 5, some concluding remarks are made.

2. Site animals

In this section a site (strongly embedded) lattice animal is specified by the set $V = \{v_1, v_2, \ldots, v_q\}$, where v_i is the number of sites in the cluster of valence (or degree) i. The maximum allowed valence is the lattice coordination number q. In the terminology of Wilkinson (1986), each A site in an A cluster is labelled in accord with the labelled code. The presence of a particular A site in the generating function for all clusters is denoted by a factor a_i, where i is the label of the site in question. The presence of a B site forming a bridge of multiplicity j is denoted in the generating function by a factor x_j.

As an example consider the symbolic representation of the general three-site A cluster in figure 1. Selection of the third-order bridge must carry a factor $a_1a_2a_3x_3$ and selection of the second-order bridge $\{i,j\}$ must carry a factor $a_ia_jx_2$. By inspection the unrestricted dummy enumerator for the cluster in figure 1 is

$$G_3(P'(\{1,2,3\})) = (1+a_1x_1[1])^{\{1\}}(1+a_2x_1[2])^{\{2\}}(1+a_3x_1[3])^{\{3\}}(1+a_1a_2x_2[1,2])^{\{1,2\}} \times (1+a_1a_3x_2[1,3])^{\{1,3\}}(1+a_2a_3x_2[2,3])^{\{2,3\}}(1+a_1a_2a_3x_3[1,2,3])^{\{1,2,3\}}. \tag{6}$$

Notice that this generating function contains *local* terms depending on some arbitrary, but explicit, labelling (see Wilkinson 1986).

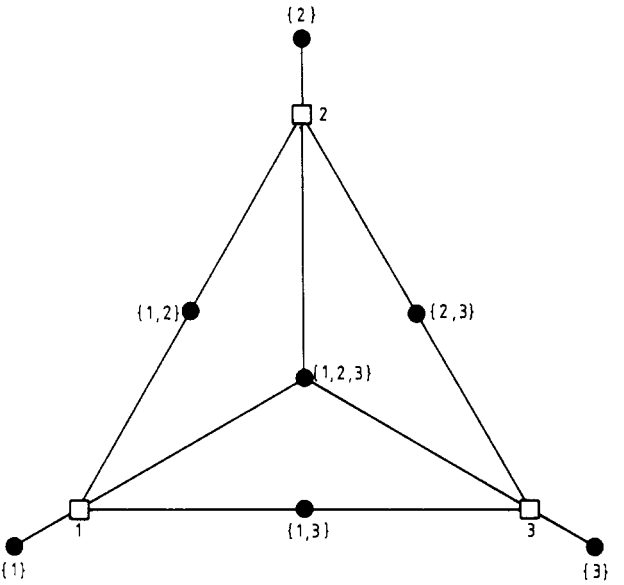

Figure 1. The general three-site A cluster. ● denote bridges and □ denote A sites.

In the general case it is evident that the substitution for this problem (following Wilkinson 1986) is

$$f(P'(\lambda_i)) = x_{|\lambda_i|}\left(\prod_{j=1}^{|\lambda_i|} a_{\varepsilon_j}\right)[\lambda_i] \tag{7}$$

where ε_j is the jth element of λ_i. Note that setting a_i to b and x_i to x, for all i, recovers equation (6) of Wilkinson (1986). For this problem there are $2^{n(A)}-1$ auxiliary polynomials:

$$\varphi_A(\lambda_i) = 1 + x_{|\lambda_i|}\left(\prod_{j=1}^{|\lambda_i|} a_{\varepsilon_j}\right) \tag{8}$$

where again, the equations of Sykes (1986a) are recovered after the above simplification and identification of the dissimilar terms.

The question now arises as to how the substitution (7) is used to obtain V. The general term in the expansion of (4) in Wilkinson (1986) has the form (using (7)) $a_{n(A)}^{p(2n)}a_{n(A)-1}^{p(2n-1)}\ldots a_2^{p(n+2)}a_1^{p(n+1)}x_{n(A)}^{p(n)}x_{n(A)-1}^{p(n-1)}\ldots x_2^{p(2)}x_1^{p(1)}$ where the variables $p(1)$-$p(n)$ are the exponents of the variables x_1-x_n respectively and $p(n+1)$-$p(2n)$ are the

exponents of the variables a_1-a_n. The valence distribution is then formed via

$$v_i = p(i) + \sum_{j=n(A)+1}^{2n(A)} \delta_{ip(j)} \tag{9}$$

where δ_{mn} is the Kronecker delta.

Using the valence distribution, the following quantities are trivially obtained:

number of sites $$s = \sum_i i v_i \tag{10}$$

number of edges (bonds) $$e = \tfrac{1}{2} \sum_i i v_i \tag{11}$$

number of cycles $$c = 1 + \tfrac{1}{2} \sum_i (i-2) v_i. \tag{12}$$

The last result follows from Euler's law of the edges. For tree topologies ($c = 0$), the number of branches also follows (see Gaunt *et al* 1984a).

Using the substitution (7) and the procedure outlined by Wilkinson (1986) enumerations have been made for lattice animals, classified by valence distribution, with up to and including thirteen sites on both the SC and BCC lattices. Clearly this constitutes an enormous amount of data, a selection of which is presented in the appendix and below. Note that the data, when regrouped to give the numbers of animals classified by bond content (i.e. c animals), confirm the values given by Sykes (1986a) and Sykes and Wilkinson (1986a) and are therefore not quoted. These data represent an extension by two terms of the one- and two-animal series for the SC lattice (Whittington *et al* 1983). The restricted site animal data for the SC lattice were known to $A_{12}(3)$, $A_{11}(4)$ and $A_{11}(5)$ (Gaunt *et al* 1980), and thus these series have been extended by one, two and two terms, respectively; namely

$$\begin{aligned} & & A_{13}(3) &= 2081\,944\,173 \\ A_{12}(4) &= 435\,360\,707 & A_{13}(4) &= 3227\,661\,914 \\ A_{12}(5) &= 445\,967\,678 & A_{13}(5) &= 3320\,593\,187. \end{aligned} \tag{13}$$

To the series for site topologies on the simple cubic lattice studied by Gaunt *et al* (1984a, b) two terms have been added, namely

$$\begin{aligned} S(12;3) &= 47\,267\,532 & S(13;3) &= 232\,773\,496 \\ S(12;4) &= 10\,604\,544 & S(13;4) &= 56\,339\,415 \\ S(12;5) &= 688\,230 & S(13;5) &= 3844\,038 \\ S(12;6) &= 10\,980 & S(13;6) &= 63\,098 \\ C(12;2) &= 94\,236\,288 & C(13;2) &= 588\,456\,696 \\ C(12;3) &= 52\,426\,416 & C(13;3) &= 453\,238\,632 \\ B(12;1,2) &= 25\,274\,544 & B(13;1,2) &= 177\,142\,404 \\ B(12;2,2) &= 1229\,124 & B(13;2,2) &= 10\,112\,880 \\ T_{12}^{(1)} &= 1296\,540 & T_{13}^{(1)} &= 5946\,168 \end{aligned} \tag{14}$$

(for notation see Gaunt *et al* (1984a, b)). Apart from unrestricted animals the only strongly embedded animal series to have been previously studied on the BCC lattice are trees (Duarte and Ruskin 1981) and c animals (Sykes 1986a). To the former, four new terms are given here and, as mentioned above, agreement is found with the latter. All other BCC data appear to be new.

The FORTRAN program used in the expansion of (7), running on the University of London's Cray 1S, achieved a counting rate of over 5000 clusters per millisecond for

Table 1. Timings for site valence program.

$n(A)$	SC	BCC
1+2	0.7s	0.8s
3	0.5s	1.4s
4	6.9s	29.5s
5	36.9s	211.3s
6	2422.2s	23 259.6s

the BCC lattice. For the SC it was about half of this. The timings are given in table 1. Although it is clear that care needs to be exercised when extrapolating these timings, it is safe to say that with current methods a large amount of computer time would be required in order to derive the data for $n = 7$.

3. Bond animals

Turning now to the problem of bond (weakly embedded) animals, consider again figure 1. Using the same notation as in the previous section, it follows by inspection that

$$\begin{aligned} G_3(P'(\{1,2,3\})) = {} & (1+a_1x_1[1])^{\{1\}}(1+a_2x_1[2])^{\{2\}}(1+a_3x_1[3])^{\{3\}} \\ & \times(1+(a_1+a_2)x_1+a_1a_2x_2[1,2])^{\{1,2\}}(1+(a_1+a_3)x_1+a_1a_3x_2[1,3])^{\{1,3\}} \\ & \times(1+(a_2+a_3)x_1+a_2a_3x_2[2,3]^{\{2,3\}})(1+(a_1+a_2+a_3)x_1 \\ & +(a_1a_2[1,2]+a_1a_3[1,3]+a_2a_3[2,3])x_2+a_1a_2a_3x_3[1,2,3])^{\{1,2,3\}}. \end{aligned} \tag{15}$$

In the general case it is evident that the substitution for this problem may be written

$$f(P'(\lambda_i)) = \sum_{\mu_j} x_{|\mu_j|}\left(\prod_{k=1}^{|\mu_j|} a_{\varepsilon_k}\right)[\mu_j] \tag{16}$$

where ε_k is the kth element of μ_j and μ_j is the jth subset of λ_i. Once again, in (16), setting a_i to b and x_i to x for all i, one recovers the substitution for bond animals classified by sites (Wilkinson 1986).

It is possible to define auxiliary polynomials as in the previous section, but now they are rather complicated. If the class (see Wilkinson 1986) under consideration consists of connected sets $S'_1, S'_2, \ldots, S'_\sigma$, and a tth-order bridge set λ_t spans some subset of $\nu = \{1, 2, \ldots, n(A)\}$, one defines the intersection sets S_i by

$$S_i = S'_i \cap \lambda_t. \tag{17}$$

If the jth subset of S_i is $\mu'_{j,i}$ (not including the empty set $\varnothing$), with elements $\varepsilon_{k,j,i}$, then the auxiliary polynomial for this bridge in this class is

$$\varphi_A = 1 + \sum_{i=1}^{\sigma} \sum_{j=1}^{2^{|S_i|}-1} x_{|\mu'_{j,i}|} \prod_{k=1}^{|\mu'_{j,i}|} a_{\varepsilon_{k,j,i}}. \tag{18}$$

Once again (18) simplifies to equation (4.1) in Sykes (1986b) when the labelling is removed. If one introduces a bond deficit, Λ_b, into the substitution by setting

$$x_{|\mu_j|} = \Lambda_b^{|\lambda_i|-|\mu_j|} \tag{19}$$

and also sets a_i to b for all i, then the bond percolation problem is recovered (Wilkinson 1986). The bond c animal series have been derived using these methods, supplemented by the techniques described in Sykes and Wilkinson (1986b), to order fourteen bonds for the BCC and SC lattices (Sykes 1986b, Sykes and Wilkinson 1986a).

The expansions detailed in Wilkinson (1986) using (16) have been carried out for small $n(A)$ and compared with published data to verify the correctness of the substitution. In applications, however, it turns out to be more efficient to enumerate, using the Martin (1974) algorithm, only those species of interest (e.g. c animals, etc). Since at the moment no application of the very detailed data produced by the present method has been made, the expansion using (16) has not been carried out to the full extent of the available labelled code data.

4. Analysis of data

One expects from RG theory that the singular parts of the generating functions for the various types of lattice animals should have the following form:

$$G(z) \sim A_1(1-\Lambda z)^{\theta-1} + A_2(1-\Lambda z)^{(\theta-1)+1} + B(1-\Lambda z)^{(\theta-1)+\Delta} + \ldots \tag{20}$$

where Δ is the first *non-analytic* correction-to-scaling exponent. If $\Delta > 1$ then the second term in (20), the *analytic* correction term, is the dominant correction. The difficulty in numerical extrapolation lies in the fact that amplitude effects may mask the true asymptotic behaviour, at least for small n. For animals with a specified topology, although (20) is presumably of the correct general form, only the dominant term in the generating function,

$$G^T(z) \sim (1-\mu z)^{-\gamma_T} \tag{21}$$

has been studied.

It is possible to fit exact enumeration data to (20) leaving all parameters free. Not surprisingly this degree of freedom results in erratic behaviour of the variables of interest. An alternative is to assume that either A_2, B or both are 0. The quality of each fit is then judged by the rate of convergence of Λ and any other parameters that are not set to 0. The best fit is assumed to be the one which most successfully mimics the (unknown) function, by virtue of successive estimates of Λ remaining the same. Such a fit is said to be 'well converged'.

For all animal varieties (other than those with specified topology) the kinds of analyses carried out are as follows (for details see the references cited): (i) biased ratio estimates (see Gaunt and Guttmann 1974), (ii) two-parameter fit with first-order analytic correction term (see Gaunt 1982), (iii) four-parameter fit with first-order non-analytic correction term (see Margolina *et al* 1983) and (iv) four-parameter fit to the exponential form (2) (see Guttmann and Gaunt 1978). Note that, loosely speaking, $t-1$ in (2) corresponds to Δ in (20). In all fits it is assumed that $\theta = \theta_0 = 1.5$ for three-dimensional animal problems.

Using the above methods of analysis it is possible to deduce reasonably precise estimates of the various growth parameters. All of the animal data in the appendix have been analysed using these methods, and in addition the bond animal data of Sykes (1986b) and Sykes and Wilkinson (1986a) have also been analysed. A typical plot (BCC lattice, unrestricted animals) of the successive values for the different analysis techniques is given in figure 2. The overall growth parameter estimates are given in table 2 where, as usual, the quoted confidence limits for each Λ represent a subjective assessment of the rate and manner of convergence.

The values of Λ for the restricted valence problem on the SC lattice are in good agreement with previously published estimates (Gaunt *et al* 1980), as are the estimates for bond and site trees (Gaunt *et al* 1982, Duarte and Ruskin 1981) and unrestricted

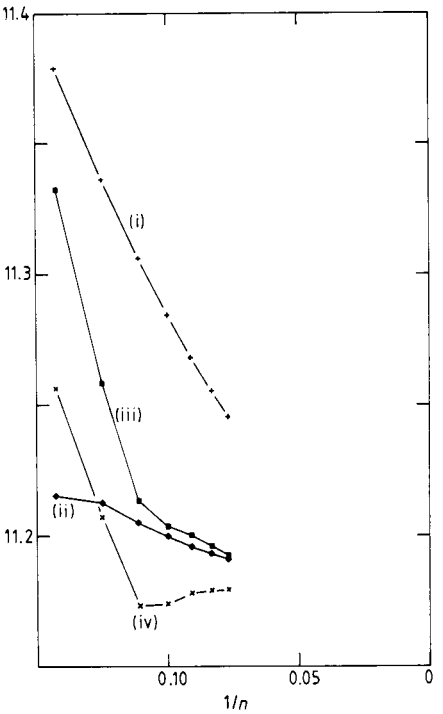

Figure 2. Estimates of $\Lambda(8)$ for site animals on the BCC lattice. The different analysis methods are discussed in the text.

bond animals (Sykes *et al* 1976) on the same lattice. The values for the restricted valence problem ($v \leqslant 7$) on the BCC lattice appear to be entirely new. The values for unrestricted bond and site animals agree with those given by Sykes *et al* (1976) and the value for site trees agrees with that given by Duarte and Ruskin (1981). Again the value for bond trees on the BCC lattice appears to be new.

It is clear that in figure 2 there is little to choose between fits (ii), (iii) and (iv), with perhaps the latter being slightly preferable to the others. This is not the situation found in general. With methods (iii) and (iv) it is only possible to estimate with any confidence values for Δ or t for restricted valence site animals. It is found that the best overall estimate is $\Delta \approx t - 1 = 1.8 \pm 0.5$. For the other problems studied Δ and t behave more erratically. In view of these facts it is impossible to decide unequivocally as to whether or not the first-order correction term in (20) is non-analytic. The rather good convergence observed in all problems for type (ii) fits suggests that if $B \neq 0$ then Δ may be close to 1. This would be in accord with the above results and the findings of Guttmann and Gaunt (1978) that for a number of three-dimensional lattices $t \approx 2$. (The situation here may be similar to that described by Rapaport (1985a, b, c) for SAW.) It should be mentioned that type (iv) estimates appear to be least well behaved in bond problems, in contrast to the excellent convergence observed in two dimensions (Guttmann 1982).

For lattice animals with specified topology the quality of the data only warrants the simplest analysis technique. For stars, combs, brushes (see Gaunt *et al* 1984a) and tadpoles (see Gaunt *et al* 1984b) biased ratio estimates have been made of the exponent γ_T, using for μ_{NAW} the SC estimate of Gaunt *et al* (1980) and the BCC estimate of

Table 2. Estimates of Λ.

	SC site	BCC site	SC bond	BCC bond
Λ_0	7.850 ± 25	10.38 ± 3	10.536 ± 10	15.124 ± 8
$\Lambda(3)$	7.875 ± 20	10.40 ± 5		
$\Lambda(4)$	8.315 ± 10	11.103 ± 10		
$\Lambda(5)$	8.350 ± 15	11.175 ± 8		
$\Lambda(6, 7)$	8.350 ± 15	11.180 ± 8	10.602 ± 12	
$\Lambda(8)$		11.180 ± 8		15.250 ± 6

Table 3. Estimates of γ_T for site animals.

Topology	Upper bound	$\gamma + b - 1$	γ_T
Star $b = 3$	3.323	3.1615	3.2 ± 0.4
Star $b = 4$	4.323	4.1615	4.0 ± 0.6
Star $b = 5$	5.4845	5.1615	4.7 ± 1.0
Star $b = 6$	6.4845	6.1615	—†
Comb $t = 2$	5.4845	5.1615	5.0 ± 2.0
Comb $t = 3$	6.646	7.1615	—†
Brush (1, 2)	6.646	6.1615	—†
Brush (2,2)	7.8075	7.1615	—†
Tadpoles:			
one-tailed	1.1615	1.1615	1.21 ± 0.12
twin-tailed	2.1615	2.1615	2.2 ± 0.5

† No estimate possible with available data.

Torrie and Whittington (1977). The results are presented in table 3 where comparison with upper bounds and the conjectured form for γ_T are made (Gaunt *et al* 1984a, b). These results lend further support to the conjecture of Gaunt *et al* (1984a, b) that $\gamma_T = \gamma + b - 1$. In addition the assumed universality between site and bond problems is also supported.

5. Conclusions

In this paper an exact enumeration study of lattice animals classified by valence distribution has been made. The enumeration method used here to derive the configurational data was the recently proposed partial generating function method of Sykes. It is generally acknowledged that a counting rate of around 200 clusters per millisecond is optimum with current direct methods. This sort of figure is, however, only applicable to the simplest enumerations. As noted by Sykes (1986a), a more realistic figure for enumerations which include a lot of detail is around five clusters per millisecond. The figure of 5000 clusters per millisecond achieved here enables useful new data to be derived and thus demonstrates the advantages of Sykes' indirect approach.

As is to be expected, the simpler the substitution for a problem, the more rapid the counting rate. This is highlighted by the reduced efficiency of the partial generating function method applied to bond animals. Contrast this with the Martin algorithm (Martin 1974), for example, where there is only a small penalty in counting bond clusters as opposed to site clusters. Nevertheless, if the detailed information produced

by classifying all bond animals according to valence distribution were required for some application, it would seem sensible to apply Sykes' method.

The results of the analyses detailed in § 4 are largely supportive of previous work; the assumptions made for the animal exponents are clearly sensible since the various extrapolations are, in the main, smooth and predictable. The inclusion of the new data for the BCC lattice confirms the universality of these exponents. Unfortunately it is difficult to draw conclusions about the nature of the first-order correction-to-scaling term, save that Δ may be close to 1. In addition the values obtained for γ_T support the conjecture of Gaunt *et al* (1984a, b).

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Appendix

Table A1. Restricted valence site animals on the BCC lattice.

n	$A(8)$	$A(7)$	$A(6)$
1	1	1	1
2	4	4	4
3	28	28	28
4	216	216	216
5	1 790	1 790	1 790
6	15 587	15 587	15 587
7	140 746	140 746	140 746
8	1 305 920	1 305 920	1 305 912
9	12 374 069	12 374 068	12 373 868
10	119 223 556	119 223 530	119 219 970
11	1 164 465 225	1 164 464 748	1 164 411 228
12	11 502 924 648	11 502 917 304	11 502 184 952
13	114 721 053 058	114 720 950 640	114 711 501 532

n	$A(5)$	$A(4)$	$A(3)$
1	1	1	1
2	4	4	4
3	28	28	28
4	216	216	216
5	1 790	1 790	1 720
6	15 587	15 531	14 180
7	140 718	139 502	119 740
8	1 305 252	1 285 788	1 036 780
9	12 362 624	12 093 424	9 156 740
10	119 056 678	115 613 338	82 168 660
11	1 162 236 984	1 120 191 264	747 057 236
12	11 474 739 560	10 976 136 968	6 867 174 742
13	114 376 908 424	108 577 531 664	63 721 448 832

Table A2. Site animals with specified topologies on the BCC lattice (for notation see Gaunt *et al* 1984a, b).

n	$S(n;3)$	$S(n;4)$	$S(n;5)$	$S(n;6)$
4	56			
5	672	70		
6	6 576	856	56	
7	55 576	9 076	664	28
8	433 632	82 160	7 296	312
9	3 161 016	686 354	68 120	3 468
10	22 154 544	5 336 336	589 768	32 608
11	149 871 264	39 721 192	4 749 384	286 344
12	990 104 880	284 314 216	36 606 160	2 340 840
13	6396 285 080	1979 428 534	271 013 960	18 349 604

n	$C(n;2)$	$C(n;3)$	$B(n;1,2)$
6	564		
7	13 752		1 032
8	204 624	7 224	30 744
9	2 434 380	266 448	503 832
10	24 867 708	5 557 560	6 507 216
11	231 031 860	85 665 528	71 276 952
12	1 993 365 228	1 104 491 472	705 261 024
13	16 303 927 104	12 530 854 416	6443 874 168

	$B(n;2,2)$	T_n	$T_n^{(1)}$
5		216	
6		1 032	396
7		5 952	2 544
8	316	32 184	19 800
9	15 292	182 352	133 392
10	285 760	972 816	884 436
11	4 076 520	5 382 120	5 508 792
12	48 156 084	28 855 320	34 198 308
13	508 560 900	157 959 216	206 159 232

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