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Bi-partite percolation and gelation

M K Wilkinson

Department of Physics, King's College, Strand, London WC2R 2LS, UK

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Abstract. Bi-partite percolation is discussed in the context of gelation. The partial generating function method is used to derive expansions for the mean number of clusters and for the weight-average molecular weight in terms of the reactant concentrations, a and b. Renormalisation group and other arguments imply that the critical behaviour in bi-partite percolation is determined by the 'ordinary' percolation fixed point at $a^* = b^* = p_c$.

1. Introduction

In this paper a discussion is given of the properties of the site percolation model on a bi-partite lattice where the sublattice sites are occupied with different probabilities a and b. This model arises naturally in the application of the partial generating function method (Sykes 1986a) to site percolation (Sykes 1986d, Sykes and Wilkinson 1986a). Here we use the formalism of Wilkinson (1986a) to produce local generating functions and thus derive expansions for the mean number of clusters and for the weight-average molecular weight (mean size) as double power series in the variables a and b.

The connection between gelation and percolation has long been known; see, for example, the recent review by Jouhier *et al* (1983). The classical theory of gelation (Flory 1941a, b, c, Stockmayer 1943, 1944) is equivalent to percolation on a Bethe pseudo-lattice and has a mean field character. Percolation on a real lattice is presumably a more suitable model of gelation because of the inclusion of the excluded volume interaction and the possibility of loops of all sizes. The correspondence is not, however, exact; one failing is that, in percolation, there is only one concentration, p, whereas in chemical gelation there is normally more than one reactant. When applying the percolation model to gelation it is therefore usually assumed that the mean ratios of reactant concentrations are the same in clusters of all sizes. It is suggested here that bi-partite percolation may be a good model for gelation especially in the case of polyfunctional condensation. There is, of course, no real difficulty if only bi-partite and ordinary percolation have the same critical behaviour, which is indeed the result found below.

The plan of this paper is as follows: in § 2 the local generating function formalism is modified for the present problem and the derived series expansions are given. In § 3 a small cell real space renormalisation group (RSRG) treatment is presented together with other arguments in favour of ordinary and bi-partite percolation having the same universality class (UC). Finally, in § 4 some concluding remarks are made.

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2. The local generating function formalism for bi-partite percolation

The site percolation problem is the most complicated problem tackled to date with the local generating function formalism. (For terminology and notation see Wilkinson (1986a).) It turns out to be completely different in character to bond percolation; there is no simple correspondence between site animals and site percolation as there is between bond animals and bond percolation (Sykes 1986c, Wilkinson 1986a). The technique described here uses the ideas of *perimeter polynomials* (Domb 1959) to calculate mean number and mean size functions for each A cluster considered as a finite graph. To do this one must consider all possible combinations of occupied and vacant sites; on an $n(A)$ site A cluster there are $2^{n(A)}$ combinations. Note that when all of the A sites are occupied the method must reduce to that for strong embeddings (Sykes 1986a, Wilkinson 1986a). The new feature in this problem is that the variables in the substitution depend on the occupancy of the sites. In particular, a factor of $(1-a)$ must be carried every time a vacant A site is selected by one or more of the bridges. Consider the cluster with $n(A)=3$ shown in figure 1. The labelled code (Wilkinson 1986a) for this cluster is $\{1\}=2, \{2\}=1, \{3\}=2, \{1,2\}=1, \{1,3\}=0, \{2,3\}=1$ and $\{1,2,3\}=1$. If all sites are occupied and if the presence of a B site is represented by a factor y, then from previous considerations (Wilkinson 1986a) the unrestricted dummy enumerator is given by

$$G_3=(1+y[1])^{\{1\}}(1+y[2])^{\{2\}}(1+y[3])^{\{3\}}(1+y[1,2])^{\{1,2\}}(1+y[1,3])^{\{1,3\}} \times(1+y[2,3])^{\{2,3\}}(1+y[1,2,3])^{\{1,2,3\}}. \tag{1}$$

Now consider the same graph with only sites 1 and 2 occupied. The unrestricted dummy enumerator is denoted by $G_{1,2,3'}$. If there were *only* two A sites then

$$G_2=(1+y[1])^{\{1\}}(1+y[2])^{\{2\}}(1+y[1,2])^{\{1,2\}}. \tag{2}$$

This now has to be generalised because sites 1 and 2 can be connected via bridge $\{1,2,3\}$ and it is necessary to record that site 3 is vacant (w_3 is used for this purpose). Thus

$$G_{1,2,3'}=(1+y[1])^{\{1\}}(1+y[2])^{\{2\}}(1+w_3y[1])^{\{1,3\}}(1+w_3y[2])^{\{2,3\}} \times(1+y[1,2])^{\{1,2\}}(1+w_3y[1,2])^{\{1,2,3\}}. \tag{3}$$

Similar considerations apply to $G_{1,2',3}$ and $G_{1',2,3}$. At this stage note that the dummy matrix is still valid if suitable correspondences are made between the occupied sites

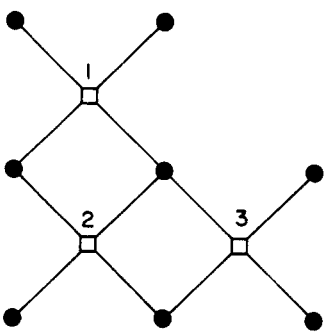

Figure 1. Example cluster.

and the dummy substitution of the same order, e.g. in (3) above one uses the dummy matrix for order 2.

When only site 1 is occupied,

$$G_{1,2',3'} = (1+y[1])^{\{1\}}(1+w_2y[1])^{\{1,2\}}(1+w_3y[1])^{\{1,3\}}(1+w_2w_3y[1])^{\{1,2,3\}} \tag{4}$$

and similarly for $G_{1',2,3'}$ and $G_{1',2',3}$.

The above equations will, as they stand, produce contributions to the mean number series. When the expansions are carried out and terms are collected then one forms an additional series (for the mean size) by weighting each term by the square of the number of occupied sites that it represents. This is accomplished by differentiation, not forgetting the presence of the A sites. For both series one recovers the required expansion variables by making the following substitutions.

(i) Set $y = b/(1-b)$.

(ii) Set $w_k^m = (1-a)$ for all $k, m \geqslant 1$.

(iii) Multiply the complete expansion by a factor $a^{|L|}(1-b)^z$, where L is the set of occupied sites and z is the number of B sites adjacent to the sites in L.

The zeroth-order contribution corresponding to no occupied A sites is

$$G_{1',\ldots,n(\mathrm{A})'} = b\Big((1-a)\sum\{i\} + (1-a)^2\sum\{i,j\} + \ldots + (1-a)^{n(\mathrm{A})}\{1,2,\ldots,n(\mathrm{A})\}\Big) \tag{5}$$

where the summations extend over all bridges of the indicated order.

It is apparent that a substitution for this problem cannot be formulated in quite the same manner as for previous problems because of the complexity of the sequence of operations. It is, however, possible to write down a general prescription for the unrestricted dummy enumerator and also to define *expanded* auxiliary polynomials (see below). Consider the set of A sites $\nu = \{1, 2, \ldots, n(\mathrm{A})\}$. As described above there are $2^{n(\mathrm{A})}-1$ cases to consider (plus the zeroth contribution, (5)). Let us call the ith subset of ν $L_i (\neq \varnothing$, the empty set for any $i)$. Let M_j be the jth subset of L_i $(j = 1, 2^{|L_i|} - |M_j| - 1)$, not including $\varnothing$ and define the set S_k as the kth subset of $\nu \backslash L_i$ $(k = 1, 2^{|\nu \backslash L_i|})$ with elements $S_{k,r}$ and also the union sets $T_{jk} = M_j \cup S_k$. Then the unrestricted dummy enumerator is given by

$$G_{n(\mathrm{A})}(L_i) = \prod_{M_i}\prod_{T_{jk}}\left(1+[M_i]y\prod_r w_{S_{k,r}}\right)^{\{T_{jk}\}} \tag{6}$$

and the expanded auxiliary polynomials are given by

$$\Phi_{n(\mathrm{A})}(L_i, M_j) = \prod_{T_{jk}}\left(1+y\prod_r w_{S_{k,r}}\right)^{\{T_{jk}\}}. \tag{7}$$

The 'expanded' polynomials are more complicated than the auxiliary polynomials encountered previously because there are several factors corresponding to more than one bridge; the one-to-one correspondence between elements of the labelled code and auxiliary polynomials has been lost.

Using the procedure outlined above all contributions to the mean number and mean size from five A sites on the SC and BCC lattices have been calculated. The calculations required 6 min of CPU time (Cray 1S) and 38 min respectively. Note that the technique described by Sykes and Wilkinson (1986a) for the determination of the mean number series is far more efficient than the present method—a point discussed further in the conclusions. The mean number expansions derived here agree with those given by Sykes and Wilkinson (1986a) and thus provide an independent check. For

the unnormalised mean size series (Sykes and Wilkinson 1986b) on the SC lattice one finds

$$\begin{aligned}S^*_{SC} &= 0.5(a+b)S_{SC}\\ &= (a+b)/2+6ab+15(a+b)ab+114a^2b^2+219(a+b)a^2b^2\\ &\quad -96(a^2+b^2)a^2b^2+1734a^3b^3+2877(a+b)a^3b^3\\ &\quad -3048(a^2+b^2)a^3b^3+25\,670a^4b^4+696(a^3+b^3)a^3b^3\\ &\quad +35\,283(a+b)a^4b^4-70\,074(a^2+b^2)a^4b^4+373\,722a^5b^5\\ &\quad +34\,050(a^3+b^3)a^4b^4+401\,283(a+b)a^5b^5-5448(a^4+b^4)a^4b^4\\ &\quad -1386\,048(a^2+b^2)a^5b^5+5479\,266a^6b^6\\ &\quad +1083\,126(a^3+b^3)a^5b^5+4104\,759(a+b)a^6b^6+\ldots. \end{aligned} \tag{8}$$

Note that not all of the contributions the method provides are quoted, only sufficient to determine the ordinary percolation series by setting $a = b$. In fact, if one wishes to numerically investigate the phase diagram then the other contributions are required (terms with small power of a and large power of b, and vice versa, see below). For the BCC lattice one finds

$$\begin{aligned}S^*_{BCC} &= 0.5(a+b)S_{BCC}\\ &= (a+b)/2+8ab+28(a+b)ab+248a^2b^2+616(a+b)a^2b^2+6512a^3b^3\\ &\quad -411(a^2+b^2)a^2b^2+13\,150(a+b)a^3b^3+168(a^3+b^3)a^2b^2\\ &\quad +159\,440a^4b^4-22\,896(a^2+b^2)a^3b^3-48(a^4+b^4)a^2b^2\\ &\quad +249\,184(a+b)a^4b^4+17\,184(a^3+b^3)a^3b^3\\ &\quad -7560(a^4+b^4)a^3b^3-889\,662(a^2+b^2)a^4b^4+4001\,552a^5b^5\\ &\quad +1923(a^5+b^5)a^3b^3+1047\,564(a^3+b^3)a^4b^4+4143\,044(a+b)a^5b^5\\ &\quad -360(a^6+b^6)a^3b^3-715\,554(a^4+b^4)a^4b^4\\ &\quad -29\,613\,488(a^2+b^2)a^5b^5+101\,014\,064a^6b^6+48(a^7+b^7)a^3b^3\\ &\quad +324\,078(a^5+b^5)a^4b^4+50\,362\,256(a^3+b^3)a^5b^5\\ &\quad +50\,830\,584(a+b)a^6b^6+\ldots. \end{aligned} \tag{9}$$

Note that extra terms have been added to (8) and (9) by calculating the undetermined coefficients from published data (Sykes *et al* 1976, Sykes and Wilkinson 1986b) and the requirement that (8) and (9) reduce to the ordinary percolation series when $a = b$.

3. Critical exponents and the bi-partite percolation phase diagram

In this section it is argued that bi-partite and ordinary percolation are in the same UC. One begins by noting some general features: it has already been mentioned that when $a = b$ ordinary percolation is recovered. Similarly when $a = 1$ or $b = 1$ the bi-partite problem is transformed into an ordinary percolation problem on a different lattice. For the simple quadratic (SQ) lattice, for example, this results in another SQ lattice but with first- and second-neighbour contacts (the square matching or SQM lattice). Another

special case is obtained if $a = 1 - b$, when AB or anti-percolation is recovered (on bi-partite lattices only). (Some relevant references are Peruggi *et al* (1984), Monroy *et al* (1982), Halley and Mai (1981) and for a recent review see Halley (1983).) AB percolation is apparently in the same UC as ordinary percolation although there is uncertainty over the triangular lattice (Halley and Mai 1981). This is of no immediate concern because the methods described here are, at present, only applicable to bi-partite lattices. Thus several points on the bi-partite percolation phase diagram are already known (figure 3) and the behaviour at these points is that of ordinary percolation. Anticipating, there is no reason to believe that there should be a change in this behaviour at other points on the critical curve.

By selecting a lattice site and considering the probability that there is a finite cluster attached to this origin (Essam 1972) it is easy to show that in one dimension the percolation probability is zero for $a, b < 1$, as in ordinary percolation. Similarly, for the Bethe lattice of coordination number 3 the equation of the critical curve is

$$4a_c b_c = 1 \tag{10}$$

and the percolation probability for A sites is

$$P_a \sim \frac{6}{(2a+1)}(1 - a_c b_c / ab) + \ldots \tag{11}$$

so that $\beta = 1$, as in the case of ordinary percolation.

Useful information about universality can be obtained from simple RG arguments. Below a small cell RSRG analysis (see, e.g., Stanley *et al* 1983) is applied to bi-partite percolation on the SQ lattice. This simple case is studied because it affords a qualitative understanding of the flows in parameter space. Following the method described by Reynolds *et al* (1977), a 3×3 group of sites is renormalised into a single site (figure 2). The criterion for the renormalised site to be occupied is that the original cluster 'spans' the cell. It is obvious that various definitions of spanning can be made, although which definition is used is thought not to matter (Reynolds *et al* 1978). If spanning is chosen to mean that there is at least one self-avoiding walk on the occupied sites going from east to west (E-W), then from a consideration of all 2^9 possible realisations of occupied and vacant sites one obtains

$$a' = (2a^2b + ab^2) + 4a^2b^2 - (2a^3b^2 + 4a^2b^3) - (5a^4b^2 + 4a^3b^3) + (2a^5b^2 + 8a^4b^3 + 4a^3b^4) - (2a^5b^3 + 4a^4b^4) + a^5b^4. \tag{12}$$

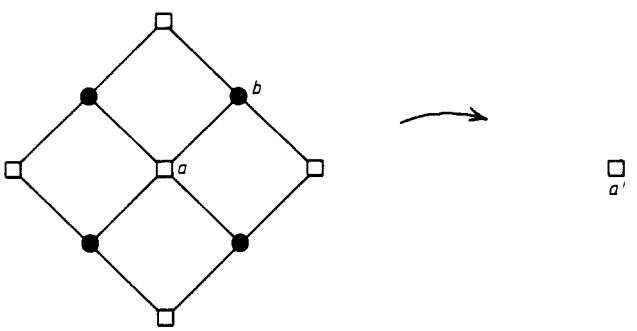

Figure 2. Cell renormalisation.

If spanning means going from (E-W) or (N-S) then

$$a' = (4a^2b + 2ab^2) + 8a^2b^2 - (20a^3b^2 + 16a^2b^3 + ab^4) + (2a^4b^2 + 20a^3b^3 + 8a^2b^4) + (2a^5b^2 + 4a^4b^3 - 8a^3b^4) - (4a^5b^3 + a^4b^4) + a^5b^4. \tag{13}$$

(Corresponding equations are obtained for b'.) Setting $a = b$ recovers the equations of Reynolds *et al* (1980).

Both (12) and (13) have trivial fixed points (FP) at $a = b = 0$ and $a = b = 1$ and non-trivial fixed points at $a^* = b^*$, where

$$\begin{aligned} a^* = b^* &= 0.619\,20 \qquad \text{(E-W)} \\ a^* = b^* &= 0.472\,63 \qquad \text{(E-W or N-S)} \end{aligned} \tag{14}$$

which should be compared with recent estimates of $p_c \approx 0.59$ (Djordjevic *et al* 1982, Derrida and de Seze 1982). Linearising about the fixed point gives

$$\begin{aligned} \nu &= 1.624 \qquad \text{(E-W)} \\ \nu &= 1.511 \qquad \text{(E-W or N-S)} \end{aligned} \tag{15}$$

which should be compared with the presumably exact value $\nu = \frac{4}{3}$ (den Nijs 1979). The phase diagram is found by iterating (12) and (13) and following the flows in parameter space. (Equation (10) is expected to be qualitatively correct.) The phase boundaries for the two definitions of spanning are shown in figure 3, together with the known points. The broken curve suggests a possible form for the exact phase boundary. (The value of p_c for SQM is taken from Essam (1972).) Notice that the line $a = 1 - b$ does not intersect the dotted curve; this is anticipated by the result that there is no AB percolation phase transition on the SQ lattice (see Halley 1983).

Note that the entire critical behaviour is determined by the ordinary percolation FP at $a^* = b^*$. Intuitively this is obvious; the recurrence relations $a' = f(a, b)$ and

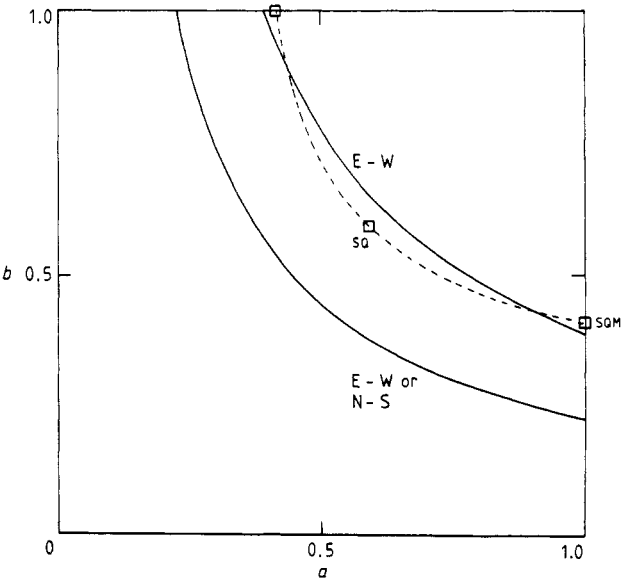

Figure 3. SQ phase diagram. □ denotes series estimates of p_c.

$b' = g(a, b)$ are completely symmetric in a and b, so one would expect any FP to lie on the line $a = b$, and this is just ordinary percolation. This observation applies to any size cell.

One may attempt to analyse (8) and (9) by approaching the critical curve along the almost perpendicular trajectory

$$b = (1 - b_0)a + b_0 \tag{16}$$

where b_0 is a constant (see Agraval *et al* 1979, Torrie *et al* 1982). Unfortunately the series now only extend to a^5 (since the lowest-order contribution from any factor just has b^n replaced by a constant). Applying the usual dlog Padé analysis (see Gaunt and Guttmann 1974) to the resulting series for both the normalised and unnormalised moments leads to estimates of γ. Naturally with so few terms the estimates show very little sign of convergence and in fact many of the approximants do not have a physical singularity. Interestingly the unnormalised moments are much better behaved than the normalised ones. Estimates of γ lie between 1 and 2 and are *consistent* with the hypothesis that ordinary and bi-partite percolation have the same UC, but the quality of the data is too poor for us to draw any stronger conclusions.

4. Conclusions

A method has been presented for the determination of percolation series expansions for bi-partite percolation based on the partial generating function method of Sykes (1986a). The particular formalism employed is that of Wilkinson (1986a). The complexity of (6) makes the method rather slow; disappointingly so when compared with the success of the method in other problems (Sykes 1986a, b, c, d, Sykes and Wilkinson 1986a, Wilkinson 1986b). When considering the mean number series Sykes and Wilkinson (1986a) avoided the complexity of (6) by a rather different approach. Work is currently in progress to extend their work to the mean size series.

Although the analyses of the two-variable series described above are by themselves inconclusive, when taken with the other evidence of § 3 there is excellent support for the contention that bi-partite and ordinary percolation have the same UC. For gels, this implies that variations in reactant concentrations are unimportant as regards critical properties.

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