Rate equation method for percolation with cluster-size-dependent dilution rates

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Abstract. Cluster-size evolution for bond dilution on a lattice is formulated as a set of rate equations for the cluster number densities. The formulation incorporates dependence of the bond removal rate on cluster size. For the Bethe lattice, the transition rates appearing in this equation are derived explicitly, yielding a tractable set of rate equations. The solution of these equations for a special case in which dilution occurs only in the infinite cluster is compared with the cluster-size distribution for Bernoulli percolation.

1. Introduction

Variants of von Smoluchowski's (1916, 1917) rate equation method for coagulation have recently been applied to various irreversible (Ziff 1980, Kang *et al* 1986) and reversible (van Dongen and Ernst 1984, Family *et al* 1986, Ernst and van Dongen 1987) aggregation processes, and to depolymerisation (bond dilution) on linear chains (Ziff and McGrady 1985, 1986). Here, the rate equation method for bond dilution is formally generalised to lattices within the framework of the kinetic theory of reversible polymerisation (van Dongen and Ernst 1984). For the Bethe lattice, combinatoric coefficients corresponding to transition rates in that theory are evaluated explicitly, and numerical results are obtained for some cases of interest.

The rate equation method is applied here to a class of bond dilution problems, including Bernoulli percolation (i.e. equal dilution rate for all bonds) as a special case. For Bernoulli percolation on the Bethe lattice, the exact solution of the cluster-size problem is known (Fisher and Essam 1961). Another case with known solutions is bond dilution on linear chains, with bond removal rates dependent on chain length and bond position within the chain (Ziff and McGrady 1985, 1986). The problems considered here involve lattices with bond removal rates dependent on cluster size. For the Bethe lattice, the rate equation formulation renders these problems computationally tractable. An explicit solution is obtained for a special case in which dilution occurs only in the infinite cluster. This solution is compared with the cluster-size distribution for Bernoulli percolation.

In the framework of reversible polymerisation theory (van Dongen and Ernst 1984), rate equations for bond dilution can be formulated for an arbitrary lattice as

$$\partial c_s/\partial t = -sR_s c_s + \sum_{i=s+1}^{x} iR_i B_{is} c_i + R_\infty p_\infty B_{\infty s}. \tag{1}$$

Here, c_s is the number density of s-clusters (i.e. the number of s-bond clusters per lattice bond), R_s is the bond removal rate from s-clusters, R_∞ is the bond removal rate from the infinite (percolating) cluster, B_{is} is the expected number of s-clusters produced by removing one bond from an i-cluster, p_∞ is the number density of bonds comprising the infinite cluster and $B_{\infty s}$ is the expected number of s-clusters produced by removing one bond from the infinite cluster.

Although site dilution is not treated explicitly here, this formulation and the results obtained therefrom are readily adapted for site dilution, or for bond dilution with cluster size based on site counting.

For Bernoulli percolation (i.e. identical removal rate $R_s(t) = R_\infty(t) \equiv R(t)$ for all bonds), the fraction p of bonds remaining in the lattice at time t is

$$p = \exp\left(-\int_0^t R(t')\,dt'\right) \tag{2}$$

based on a non-diluted lattice ($p = 1$) initially. Equation (2) establishes the correspondence, for Bernoulli percolation, between the dynamic formulation, (1), and the usual static problem parametrised by p. Other bond dilution processes cannot always be formulated as static problems, though the processes analysed here can be so formulated.

For Bernoulli percolation on finite-dimensional lattices, p_∞ is a familiar quantity (Stauffer 1985), but little is known about the quantities $B_{\infty s}$ or B_{is}. $B_{\infty s}$ must depend on p since it is zero for all s when $p = 1$, but non-zero for $p_c \leqslant p < 1$ (p_c is the percolation threshold). Likewise, B_{is} must depend on p. For instance, $B_{s+1,s}$ depends on the expected number of bonds adjacent to the perimeter of an $(s+1)$-cluster, which is p-dependent (Stauffer 1985) (e.g. compare percolation clusters ($p = p_c$) with lattice animals ($p \to 0$)). The p dependences of $B_{\infty s}$ and B_{is} for Bernoulli percolation on finite-dimensional lattices are unknown. Even if they were known, these p dependences would not necessarily apply to other bond dilution processes, so (1) may not be useful for analysing the more general class of bond dilution processes on finite-dimensional lattices.

For Bernoulli percolation on the Bethe lattice with coordination number z, an implicit expression for $p_\infty(p)$ is available (Fisher and Essam 1961), and expressions for $B_{\infty s}$ and B_{is} can be derived, as demonstrated shortly. Furthermore, the expressions are valid for the general class of problems represented by (1). This is a consequence of the fact that all Bethe lattice clusters of given size s have equal perimeters, of size $u = z + (z-2)s$ (Fisher and Essam 1961). s and u are the only cluster properties determining the relative contributions of cluster configurations to the sources and sinks in (1), so all cluster configurations for given s are equally likely, as for Bernoulli percolation (Fisher and Essam 1961). It also follows that the quantities B_{is} are purely combinatoric for the Bethe lattice and therefore independent of p. On the other hand, $B_{\infty s}$ is still p dependent because it must still be zero for all s at $p = 1$ but non-zero for $p_c \leqslant p < 1$.

Turning therefore to Bernoulli percolation on the z-coordinated Bethe lattice, the time derivative of (2) gives $dp/dt = -R(t)p$, so that (1) becomes

$$-p\frac{\partial n_s}{\partial p} = -sn_s + \sum_{i=s+1}^{\infty} iB_{is}n_i + p_\infty B_{\infty s}. \tag{3}$$

Here and henceforth, n_s is used in place of c_s to denote the number density of s-clusters for the special case of Bernoulli percolation. In § 3, $h_s = c_s - n_s$ denotes the deviation of the number density for a non-Bernoulli case from the Bernoulli solution. The minus

sign on the left-hand side of (3) reflects the reduction of p from its initial value $p_0 = 1$ as bond dilution proceeds.

2. Transition rates for the Bethe lattice

Recall that the transition rate B_{is} is defined as the expected number of s-clusters produced by removing one bond from an i-cluster. In accordance with the prescription of van Dongen and Ernst (1984), this quantity is derived by constructing i-clusters with s bonds on one side of a given bond and $i - s - 1$ bonds on the other side of that bond. (Such a cluster will yield an s-cluster and an $(i - s - 1)$-cluster when the given bond is removed.) Since all configurations of an i-cluster are equally likely, B_{is} is equal to twice the number of distinct configurations thus obtained, divided by the total number K_i of distinct i-cluster configurations containing a given bond. (The factor of two appears because the s-cluster may occur on either side of the given bond or, for the case $i = 2s + 1$, on both sides. K_i corresponds to the quantity ib_i of Fisher and Essam (1961).) Thus

$$B_{is} = 2Q_{s+1}Q_{i-s}/K_i \tag{4}$$

where Q_{s+1} denotes the number of distinct configurations consisting of s bonds on one side of a given bond.

Q_{s+1} is evaluated using a recursion relation. Van Dongen and Ernst (1984) have indicated how such a recursion relation can be constructed for general polymer configurations. Here, their approach is applied to loopless configurations with maximum coordination z at any node, i.e. to bond clusters on the z-coordinated Bethe lattice. For this case, an explicit solution of the recursion relation is obtained.

Each configuration contributing to Q_{s+1} consists of the given bond and $z - 1$ 'subclusters' attached to one side of that bond. These subclusters contain, respectively, $s_1, s_2, \ldots, s_{z-1}$ bonds, where $\sum_{j=1}^{z-1} s_j = s$. Empty subclusters are allowed, so s_j ranges from 0 to s. Each non-empty subcluster is analogous to the original set of $s + 1$ bonds in that it consists of a bond and $z - 1$ subclusters attached to that bond. Therefore the specification of configurations contributing to Q_{s+1} is applicable to non-empty subclusters, namely there are Q_{s_j} distinct subclusters consisting of s_j bonds. The enumeration is extended to empty subclusters in a consistent manner by setting $Q_0 = 1$. The number Q_{s+1} of distinct configurations is the product of the number of distinct configurations of the $z - 1$ subclusters, summed over the allowed values of $s_1, s_2, \ldots, s_{z-1}$. Thus

$$Q_{s+1} = \sum_{s_1=0}^{s} \sum_{s_2=0}^{s} \cdots \sum_{s_{z-1}=0}^{s} \delta_{s_1+s_2+\ldots+s_{z-1},s} Q_{s_1} Q_{s_2} \cdots Q_{s_{z-1}}. \tag{5}$$

Here, Kronecker delta notation is employed to incorporate the constraint $\sum_{j=1}^{z-1} s_j = s$.

To evaluate Q_s using (5), that equation is expressed in terms of the generating function $g(w) \equiv \sum_{s=1}^{\infty} Q_s w^s$ by multiplying the equation by w^{s+1} and summing over s ranging from 0 to ∞. Recalling that $Q_0 = 1$, this gives

$$g = w(1 + g)^{z-1}. \tag{6}$$

Motivated by Fisher and Essam's (1961) method for evaluating the quantity K_i, Q_s is

evaluated by exploiting the identity

$$Q_s = \frac{1}{2\pi i} \oint \left(\sum_{j=1}^{\infty} Q_j w^j \right) w^{-(s+1)} \, dw = \frac{1}{2\pi i} \oint g w^{-(s+1)} \, dw. \tag{7}$$

This identity follows from the residue theorem, regarding w as a complex variable and taking the contour of integration to be a small closed loop encircling the origin. Near the origin, the analytic behaviour of g is the same as that of w. Therefore a change of variables based on (6) and its derivative:

$$\frac{dg}{dw} = \frac{(1+g)^z}{1-(z-2)g} \tag{8}$$

gives

$$Q_s = \frac{1}{2\pi i} \oint (1+g)^{(z-1)s-1}[1+(2-z)g]g^{-s} \, dg. \tag{9}$$

The residue is evaluated by expanding the first factor in the integrand in a power series in g. The final result is $Q_1 = 1$ and

$$Q_s = \frac{z-1}{s-1} \binom{(z-1)s-1}{s-2} \tag{10}$$

for $s > 1$.

B_{is} can now be evaluated by substituting (10) into (4) and using Fisher and Essam's (1961) result:

$$K_s = \frac{2s}{(s+1)[(z-1)s+z]} \binom{(z-1)s+z}{s}. \tag{11}$$

Having thus determined B_{is}, the quantity $p_\infty B_{\infty s}$ can be determined from (3) based on the expression (Fisher and Essam 1961)

$$sn_s = K_s p^s (1-p)^{z+(z-2)s} \tag{12}$$

for the cluster-size distribution for Bernoulli percolation on the Bethe lattice. Using (4) and (12), the sum in (3) can be expressed as

$$\sum_{i=s+1}^{\infty} i B_{is} n_i = 2Q_{s+1}(1-p)^z w^s g(w) \tag{13}$$

where

$$w = p(1-p)^{z-2}. \tag{14}$$

An ambiguity has been introduced in that (6) for $g(w)$ has two positive solutions for $0 < w < (z-2)^{z-2}/(z-1)^{z-1}$. ($w$ falls within this range for $0 < p < 1$ except that it equals the upper bound at $p = p_c = 1/(z-1)$.) For w given by (14), $g = p/(1-p)$ satisfies (6). Following Fisher and Essam (1961), the appropriate root of (6) is obtained for all p by choosing $g = p^*/(1-p^*)$, where p^* is the root of $p^*(1-p^*)^{z-2} = p(1-p)^{z-2}$ that vanishes continuously as $p \to 0$ or $p \to 1$. For $p < p_c$, this gives $p^* = p$.

Finally, evaluation of the p derivative of n_s and rearrangement of terms in (3) gives

$$p_\infty B_{\infty s} = [z+(z-2)s] \frac{pn_s}{1-p} - 2Q_{s+1}(1-p)^z w^s g(w). \tag{15}$$

Since p_∞ can likewise be expressed in terms of p^* (Fisher and Essam 1961), the prescription for $B_{\infty s}$ is complete. It is readily verified that the right-hand side of (15) vanishes for $g = p/(1-p)$, consistent with the choice of this root of (6) for $p < p_c$. In fact, imposition of the requirement that $p_\infty B_{\infty s}$ must vanish for $g = p/(1-p)$ provides an alternate method for deriving (10) without using contour integration.

3. The generalised bond dilution problem

To analyse the generalised bond dilution problem, (1), with arbitrary removal rates $R_s(t)$, it is convenient to reparametrise that problem in terms of the quantity

$$p = \exp\left(-\int_0^t R_\infty(t')\, dt'\right) \tag{16}$$

which is the fraction of bonds that would remain in the lattice at time t if $R_s(t)$ were equal to $R_\infty(t)$ for all s. Thus, the structure of the infinite cluster for given p is the same as for Bernoulli percolation with a fraction p of the bonds remaining. Based on (16), (1) can be expressed as

$$-p\partial c_s/\partial p = -sr_s c_s + \sum_{i=s+1}^{\infty} i r_i B_{is} c_i + p_\infty B_{\infty s} \tag{17}$$

where $r_s(t) = R_s(t)/R_\infty(t)$.

Defining h_s by the relation $c_s = n_s + h_s$, subtraction of (3) from (17) gives

$$-p\partial h_s/\partial p = -s(r_s c_s - n_s) + \sum_{i=s+1}^{\infty} i B_{is}(r_i c_i - n_i) \tag{18}$$

thus eliminating the infinite-cluster term. This reduces to a solvable system of equations for at least three cases: (i) $r_i = 1$ for all $i > I$, in which case $c_i = n_i$ for all $i > I$ so the upper limit of the sum becomes I, (ii) $r_i = 0$ for all $i > I$, in which case the infinite sum can be evaluated using (13), and (iii) $z = 2$ (the linear chain), for which explicit solutions have been obtained by Ziff and McGrady (1985, 1986) for various functional dependences of r_i on i.

A case of particular interest is $r_i = 0$ for all i, i.e. the case in which bond dilution occurs only in the infinite cluster. In this case, c_s is the size distribution of the 'primary fragments' which evolve from the infinite cluster during bond dilution. This dilution process may represent, e.g., depolymerisation of a bulk macromolecular material into fragments that rapidly escape by evaporation into an environment in which further degradation is inhibited. For this case, (18) reduces to

$$-p\partial h_s/\partial p = sn_s - \sum_{i=s+1}^{\infty} i B_{is} n_i = sn_s - 2Q_{s+1}(1-p)^z w^s g \tag{19}$$

where (13) has been used to evaluate the sum.

Equation (19), in conjunction with (6), (10), (11), (12) and (14), can be integrated numerically for any s. For coordination number $z = 3$, (6) can be solved explicitly for $g(w)$, giving

$$g = \frac{1 - 2w - (1 - 4w)^{1/2}}{2w} = \frac{1-p}{p} \tag{20}$$

where the final expression, valid for $p \geq p_c$, follows from (14). (The root of (6) is selected that is consistent with Fisher and Essam's (1961) result $p^* = 1 - p$ above $p = p_c$ for $z = 3$, where p^* is defined after (14).) Using (20), (19) can be integrated analytically.

For $p = 1$, $h_s = 0$ for all s. Since bond dilution ceases at the percolation threshold $p_c = 1/(z-1)$, it is interesting to compute the quantities h_s at $p = p_c$. For $z = 3$, integration of (19) from $p_c = \frac{1}{2}$ to p gives

$$h_s(p_c) = K_s \left(\Pi_{s+3}(s-1, s+3) - \sum_{j=0}^{s+3} 2^{-(2s+3-j)} \Pi_j(s-1, s+3) \right)$$

$$- 2Q_{s+1} \left(\Pi_{s+4}(s-2, s+4) - \sum_{j=0}^{s+4} 2^{-(2s+3-j)} \Pi_j(s-2, s+4) \right) \tag{21}$$

where

$$\Pi_j(n, m) = \frac{1}{m+1} \prod_{k=0}^{j} \frac{m+1-k}{m+n+1-k}. \tag{22}$$

This result is obtained using the relation (Gradshteyn and Ryzhik 1980)

$$\int x^n (1-x)^m \, dx = x^{n+1} \sum_{j=0}^{m} (1-x)^{m-j} \Pi_j(n, m). \tag{23}$$

Numerical results based on (21) are shown in figure 1. $h_s(p_c)$ is negative for small s and increases with increasing s until it becomes positive, peaks, and finally decays. Thus, suppression of finite-cluster bond dilution shifts the cluster-size distribution toward the larger sizes, as one would expect. For the range of s shown in figure 1, $h_s(p_c)$ is much smaller in magnitude than $n_s(p_c)$. However, $h_s(p_c)$ converges to $n_s(p_c)$ in the large-s limit, i.e. $c_s(p_c) \to 2n_s(p_c)$ for large s.

The latter result is derived by substituting (12) and the relation

$$Q_{s+1} = \frac{(z-2)(s+1)+2}{2s} K_s \tag{24}$$

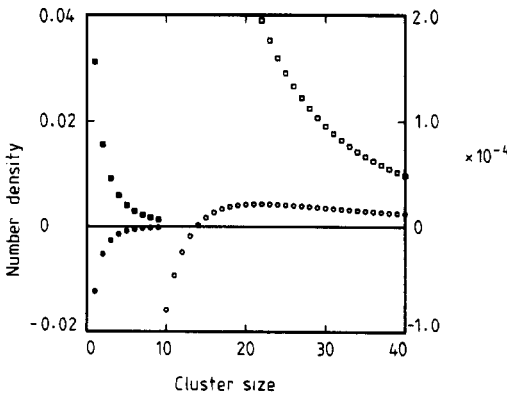**Figure 1.** Cluster number densities n_s (squares) and $h_s = c_s - n_s$ (circles) at the percolation threshold plotted against cluster size s. n_s and c_s are the respective number densities for Bernoulli percolation and for bond dilution restricted to the infinite cluster. Computed results are for bond dilution on the Bethe lattice with coordination number $z = 3$. Full and open symbols correspond to the axis scalings on the left-hand and right-hand sides, respectively. (For $s \geq 10$, the vertical scale is expanded by a factor of 200.)

based on (10) and (11), into (15). For $z = 3$, this yields

$$p_x B_{x s} = \frac{2p - 1}{p(1 - p)} \, s n_s = -\frac{\mathrm{d} n_s}{\mathrm{d} p} \tag{25}$$

to leading order in $s \gg 1$, where the rightmost equality follows from (12). For $r_i = 0$, substitution of this expression into (17) gives $p \, \mathrm{d} c_s / \mathrm{d} p \approx \mathrm{d} n_s / \mathrm{d} p$ for $s \gg 1$, or

$$c_s(p_c) \approx - \int_{p_c}^{1} \frac{\mathrm{d} n_s}{\mathrm{d} p} \frac{\mathrm{d} p}{p}. \tag{26}$$

For $s \to \infty$, the main contribution to the integral comes from $p \approx p_c$ because the large-cluster number density falls off most rapidly near p_c. (This follows from asymptotic analysis of (12).) Therefore $c_s(p_c) \approx n_s(p_c)/p_c = 2 n_s(p_c)$ for large s, as claimed.

4. Extensions

Finally, further generalisations of the bond-dilution problem are noted. For the Bethe lattice, consideration has been restricted thus far to an initial state in which all bonds are intact. The results presented here are readily generalised to an arbitrary initial size distribution, provided that the ensemble of clusters for any given size s is the same as that for Bernoulli percolation, i.e. all distinct s-clusters containing a given bond are equally probable.

Another generalisation is motivated by the aforementioned interpretation of the bond-dilution process as depolymerisation in a condensed phase, say a polymer melt, but now with the process of evaporative escape of finite clusters occurring at a finite size-dependent rate $E_s(t)$. c_s is now interpreted as the size distribution of finite clusters remaining in the melt. This process can be represented by subtracting $\Sigma_s E_s c_s$ from the right-hand side of (1). If $E_s = 0$ for s exceeding some maximum value S, then a closed set of rate equations for $s \le S$ can be obtained. The incorporation of this formulation into a phenomenological model of volatile species escape during coal pyrolysis will be reported elsewhere.

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