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Abstract. The momentum space renormalisation group is applied to a Hamiltonian which describes site-bond correlated percolation, which in turn models the sol–gel transition when solvent effects are present. Mean field theory is used to determine the qualitative features of the phase diagram which includes sol and gel phases in either one- or two-phase regions. Recursion relations in $d = 6 - \epsilon$ dimensions are derived and are shown to have a fixed point corresponding to simultaneous gelation and phase separation. At this fixed point, the critical exponents describing phase separation are the same as for the Ising model $\nu_0 = \frac{1}{2}$, $\eta = 0$ for $d > 4$ whereas those describing gelation differ from those for the usual percolation problem: $\nu_1 = 2/(d-2)$, $\eta_1 = 0$ for $4 < d < 6$.

In the site percolation problem, sites are occupied at random and clusters consist of groups of nearest-neighbour occupied sites; in bond percolation, bonds are occupied at random and clusters consist of sites connected by occupied bonds (Essam 1973, Stauffer 1979). Recently, site-bond correlated percolation has been proposed (Coniglio *et al* 1979) as a model for reversible sol–gel phase transitions (Tanaka *et al* 1979). In this model, sites can be vacant or occupied with probabilities determined by thermal equilibrium Boltzmann factors as in a lattice gas or Ising model. Bonds between nearest-neighbour occupied sites can form with probability p_B. One then considers bond percolation among the occupied sites. Unoccupied sites correspond to solvent molecules, occupied sites to monomers that can be chemically bonded to form a gel. Percolation among the occupied sites corresponds to gelation. It has been shown (Murata 1979, Coniglio and Klein 1979 (unpublished)) that the correlated site-bond model can be obtained from the one-state limit of the diluted s-state Potts model. In this model, each site, x, on a d-dimensional lattice has associated with it a Potts variable $\sigma(x) = 1, \ldots, s$ and a lattice gas variable $n(x) = 0, 1$. The Hamiltonian is

$$-\beta\mathcal{H} = J \sum_{\langle x,x' \rangle} n(x)n(x')[s\delta_{\sigma(x)\sigma(x')} - 1] + K \sum_{\langle x,x' \rangle} n(x)n(x') - \Delta \sum_x n(x)$$

$$+ H \sum_x n(x)[s\delta_{\sigma(x)1} - 1] \tag{1}$$

where K is the lattice gas nearest-neighbour constant, Δ is the chemical potential for occupied sites, and J is related to the probability p_B that a bond between occupied sites

is present via the relation $p_B = 1 - e^{-J}$. An interesting property of the Hamiltonian (1) is that for $J = \frac{1}{2}K$, it becomes equivalent to the $(s+1)$-state Potts Hamiltonian, which becomes equivalent to the lattice gas Hamiltonian when $s \to 1$. Consequently, one expects the percolation critical point that occurs as J is varied keeping $K = 2J$ to have Ising symmetry. The Migdal renormalisation group procedure (Migdal 1975, Kadanoff 1976) has been applied to Hamiltonian (1) (Coniglio and Klein 1979 (unpublished)).

In this paper, we will study correlated site-bond percolation within the context of the ϵ expansion (Wilson and Fisher 1972) with particular emphasis on the critical point where the percolation and lattice gas variables order simultaneously. In order to express the partition function for the Hamiltonian (1) in field theoretic form, we first rewrite (1) as

$$-\beta \mathcal{H} = J \sum_{\langle x,x' \rangle} b_l(x)b_l(x') + \bar{K} \sum_{\langle x,x' \rangle} s(x)s(x') + h \sum_x s(x) + \sum_{x,l} H_l b_l(x) + \text{constant} \tag{2}$$

where summation over repeated l indices is understood, $\bar{K} = \frac{1}{4}K$, $h = \frac{1}{2}(\frac{1}{2}zK - \Delta)$ where z is the coordination number of the lattice, $s(x) = 2n(x) - 1$, $b_l(x) = n(x) e_l^{\sigma(x)}$ where $e_l^{\sigma(x)}$ satisfy the relations (Zia and Wallace 1975)

$$\sum_\sigma e_l^\sigma e_{l'}^\sigma = s\delta_{ll'} \qquad \sum_l e_l^\sigma e_{l'}^\sigma = (s\delta_{\sigma\sigma'} - 1) \tag{3}$$

and where $H_l = He^1{}_l$.

Using the Hubbard–Stratanovich transformation and appropriately shifting variables (see, for example, Amit 1978), the partition function for equation (2) can be written as

$$Z = C \exp\left[-\frac{1}{2} \sum_{x,x'} (H_l(x)J^{-1}(x,x')H_l(x') + h(x)\bar{K}^{-1}(x,x')h(x')) \right] Z' \tag{4}$$

$$Z' = \int \mathscr{D}\phi_l \mathscr{D}\phi_0 \exp\left[-\frac{1}{2} \sum_{x,x'} (\phi_l(x)J^{-1}(x,x')\phi_l(x') + \phi_0(x)\bar{K}^{-1}(x,x')\phi_0(x')) \right]$$

$$\times \exp\left[\sum_{x,x'} (H_l(x)J^{-1}(x,x')\phi_l(x') + h(x)\bar{K}^{-1}(x,x')\phi_0(x')) \right] \exp\left(\sum_x v(x) \right)$$

where c is a constant and

$$\exp(v(x)) = \text{Tr}_{\sigma(x)}[\exp(\phi_l(x)e_l^{\sigma(x)}) \exp(\phi_0(x)) + \exp(-\phi_0(x))]. \tag{5}$$

Expectation values of $\phi_l(x)$ and $\phi_0(x)$ are related to $b_l(x)$ and $S(x)$ via

$$\langle b_l(x) \rangle = \frac{\partial \ln Z}{\partial H_l(x)} = \sum_{x'} J^{-1}(x,x')(\langle \phi_l(x') \rangle - H_l(x'))$$

$$\langle S(x) \rangle = \frac{\partial \ln Z}{\partial h(x)} = \sum_{x'} \bar{K}^{-1}(x,x')(\langle \phi_0(x) \rangle - h_0(x)). \tag{6}$$

Going to the continuum limit and retaining only the leading terms in ϕ_l and ϕ_0, we obtain

$$Z' = \int \mathscr{D}\phi_l \mathscr{D}\psi_l \exp(-\beta \bar{\mathcal{H}}) \tag{7}$$

where

$$\beta \bar{\mathcal{H}} = \frac{1}{2} \int d^d x \left[r_1 \sum_l \phi_l^2 + \sum_l (\nabla \phi_l)^2 + r_0 \phi_0^2 + (\nabla \phi_0)^2 \right] - \int d^d x [h(x)\phi_0(x) + H_l(x)\phi_l(x)]$$

$$- \frac{1}{3!} w\lambda_{l_1 l_2 l_3} \int d^d x \, \phi_{l_1}(x)\phi_{l_2}(x)\phi_{l_3}(x)$$

$$- \frac{1}{2}w_2 \int d^d x \, \phi_0(x) \sum_l \phi_l^2(x) + u_1 \int d^d x \, \phi_0^4(x) \tag{8}$$

where $r_1 = z(1 - \frac{1}{2}zJ)$, $r_0 = z(1 - \bar{K}z)$, $w_1 = \frac{1}{2}a^{d/2}z^3 J^{3/2}$, $w_2 = \frac{1}{2}a^{d/2}z^3\bar{K}^{1/2}J$ and $u_1 = \frac{1}{12}a^d z^4 \bar{K}^2$ where a is a lattice constant, and where external fields have been rescaled via $h = a^{-d/2}J^{-1/2}h$ and $H = a^{-d/2}\bar{K}^{-1/2}H$. Finally,

$$\lambda_{l_1 l_2 l_3} = \sum_\sigma e_{l_1}^\sigma e_{l_2}^\sigma e_{l_3}^\sigma. \tag{9}$$

The free energy, F, in mean field theory is obtained by ignoring spatial fluctuations in ϕ_0 and ϕ_l and setting $\phi_l = e_l^1 \phi$:

$$F = \frac{\beta \bar{\mathcal{H}}}{\Omega} = \frac{1}{2}(s-1)r_1\phi^2 - \frac{1}{3!}w_1(s-1)(s-2)w_1\phi^3$$

$$- \frac{1}{2}w_2(s-1)\phi_0\phi^2 + \frac{1}{2}r_0\phi_0^2 + u_1\phi_0^4 - (s-1)H\phi - h\phi_0 \tag{10}$$

where Ω is the volume.

In the limit $s \to 1$, we obtain the following equations of state:

$$h = \phi_0^3 \left[4u_1 + \frac{r_0}{\phi_0^2} \right] \tag{11}$$

$$H = \phi^2 \left(\frac{1}{2}w_1 + \frac{r_1 - w_2\phi_0}{\phi} \right). \tag{12}$$

Note that equation (11) is the mean field equation of state for the Ising model and is completely independent of the percolation variables. For $h = 0$, the Ising order parameter satisfies

$$\phi_0 = \begin{cases} \pm \left(\dfrac{-r_0}{4u_1} \right)^{1/2} & r_0 < 0 \\ 0 & r_0 > 0 \end{cases} \tag{13}$$

whereas the percolation (or gel) order parameter (fraction of sites in the infinite cluster) satisfies

$$\phi = \begin{cases} \dfrac{2}{w_1}(w_2\phi_0 - r_1) & r_1 < w_2\phi_0 \\ 0 & r_1 > w_2\phi_0. \end{cases} \tag{14}$$

The phase diagram implied by equations (13) and (14) is shown in figure 1. Note that there is a one-phase region and a two-phase region (solvent-rich and solvent-poor) and that in both regions both sol and gel phases exist. The percolation (gelation) threshold occurs at $r_1 = w_2\phi_0$. The mean cluster size (clusters are occupied sites connected by
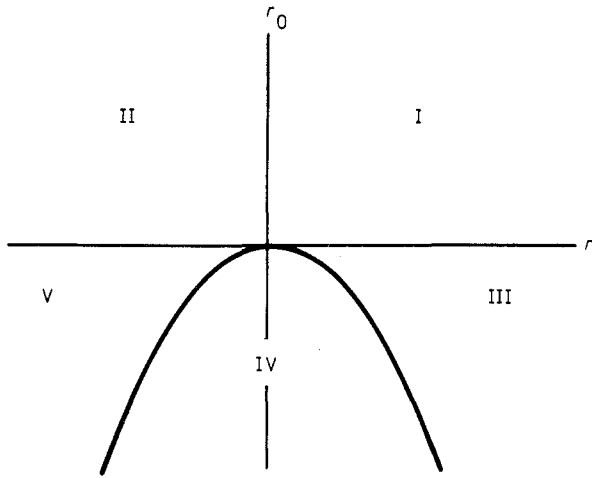
Figure 1. Phase diagram corresponding to equations (13) and (14). Region I is a single-phase sol, region II a single-phase gel, region III a two-phase sol, region IV a solvent-rich sol coexisting with a solvent-poor gel, and region V two coexisting gel phases.

occupied bonds), S, diverges at threshold as

$$S = \left(\frac{\partial H}{\partial \phi}\right)^{-1} = |r_1 - w_2 \phi_0|^{-1}. \tag{15}$$

If we choose $r_0 = r_1$ which corresponds to $J = \frac{1}{2}K$, the gelation (percolation) curve is $r_0 = w_2 \phi_0$ (see figure 2). Note that the gelation curve terminates at the Ising critical point as expected. The mean field critical exponents for gelation are the same as those for percolation on an undiluted lattice ($\gamma_p = 1$, $\beta_p = 1$, $\eta_p = 0$) all along the gelation curve including where it intersects the Ising critical point in agreement with results on the Bethe lattice (Coniglio *et al* 1979). Note also that if r_1 is fixed at some value other than r_0, and r_0 is varied, the gelation curve no longer intersects the Ising critical point in agreement with experimental results (Tanaka *et al* 1979).
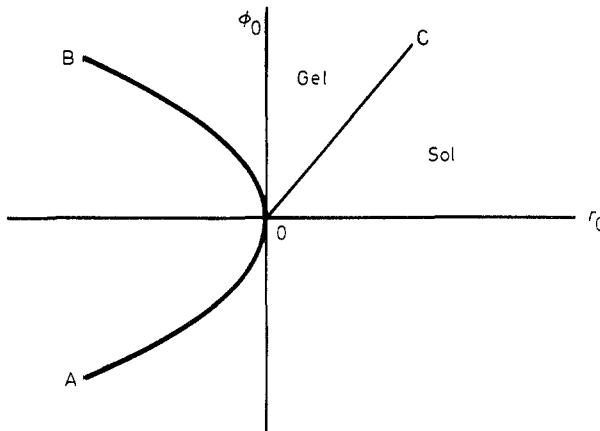

Figure 2. Co-existence curve (AOB) and gelation curve (OC) for the binary mixture with $r_1 = r_0$. $\phi_0 = r_0/w_2$.

Recursion relations for the potentials in equation (9) in $6 - \epsilon$ dimensions can be developed in the standard way (Wilson and Kogut 1974, Wegner and Houghton 1973, Rudnick and Nelson 1976). For simplicity, we consider only the disordered regime with H and $h = 0$ (region I in figure 1). We obtain in the limit $s \to 1$

$$\frac{\mathrm{d}r_0}{\mathrm{d}l} = (2 - \eta_0)r_0 \tag{16a}$$

$$\frac{\mathrm{d}r_1}{\mathrm{d}l} = (2 - \eta_1)r_1 + \tfrac{1}{2}w_1^2 K_6 \left(\frac{1}{1+r_1}\right)^2 - w_2^2 K_6 \left(\frac{1}{1+r_0}\right)\left(\frac{1}{1+r_1}\right) \tag{16b}$$

$$\frac{\mathrm{d}w_1}{\mathrm{d}l} = \tfrac{1}{2}(\epsilon - 3\eta_1)w_1 - 2w_1^3 K_6 \left(\frac{1}{1+r_1}\right)^3 + 3w_1 w_2^2 K_6 \left(\frac{1}{1+r_1}\right)^2 \left(\frac{1}{1+r_0}\right) \tag{16c}$$

$$\frac{\mathrm{d}w_2}{\mathrm{d}l} = \tfrac{1}{2}(\epsilon - 2\eta_1 - \eta_0)w_2 + w_2^3 K_6 \left(\frac{1}{1+r_1}\right)^2 \left(\frac{1}{1+r_0}\right) - w_1^2 w_2 K_6 \left(\frac{1}{1+r_1}\right)^3 \tag{16d}$$

where $\eta_0 = 0$, $\eta_1 = \tfrac{1}{3}K_6(w_2^2 - \tfrac{1}{2}w_1^2)$ and $K_d = 2^{-(d-1)}\pi^{-d/2}$. In general, one might expect an additional third-order term, $(1/3!)w_3\phi_0^3$, to develop on iteration of the renormalisation procedure. When $H = 0$, no such term develops in the limit $s \to 1$. Note that the equation for r_0 completely decouples from the other equations leading to a mean field correlation length exponent, $\nu_0 = \tfrac{1}{2}$. Equations (16) have three fixed points: (i) the percolation fixed point (Harris *et al* 1975) with $w_2 = 0$, $K_6 w_1^2 = 2\epsilon/7$ and percolation correlation length exponent $\nu_1^{-1} = 2 - 5\epsilon/21$, (ii) an unphysical fixed point with $w_1 = 0$ and $K_6 w_2^2 = -\epsilon$, and (iii) a new fixed point corresponding to simultaneous gelation and phase separation with

$$K_6 w_1^2 = \epsilon \qquad K_6 w_2^2 = \tfrac{1}{2}\epsilon$$

$$\eta_1 = 0 \qquad \nu_0 = \tfrac{1}{2} \qquad \nu_1^{-1} = 2 - \frac{\epsilon}{2} = \frac{d-2}{2}. \tag{17}$$

Though equations (17) are valid only to first order in ϵ, we believe that $\nu_1 = 2/(d-2)$ for all $4 \le d \le 6$. The argument proceeds as follows. The scaling exponent for the field ϕ_0 is $x_0 = \tfrac{1}{2}(d-2)$ and for $\Sigma_l \phi_l^2$ is $d - 1/\nu_1$. The quantity $w_2\phi_0 \Sigma_l \phi_l^2$ must scale as the inverse volume (i.e. with exponent d). w_2 reaches a constant value at the fixed point so that it does not change under rescaling. Thus, assuming that the scaling exponent for $\phi_0 \Sigma_l \phi_l^2$ is the sum of those for ϕ_0 and $\Sigma_l \phi_l^2$, we obtain

$$\tfrac{1}{2}(d-2) + (d - \nu_1^{-1}) = d \qquad \text{or} \qquad \nu_1 = \frac{2}{d-2} \tag{18}$$

in agreement with the results of the ϵ expansion. The crucial assumption, here, is that $\phi_0 \Sigma_l \phi_l^2$ could be decomposed into independent parts ϕ_0 and $\Sigma_l \phi_l^2$. We believe this decomposition is valid for $d > 4$. At $d = 4$, ϕ_0 begins to scale non-classically and the relation $\nu_1 = 2/(d-2)$ probably breaks down.

Equations $(16a)$ and $(16b)$ determine scaling in the variables r_0 and r_1. Linearising in the vicinity of the critical point, we obtain

$$\frac{\mathrm{d}t_i}{\mathrm{d}l} = \sum_{j=0,1} M_{ij}t_j \tag{19}$$

where $i, j = 0, 1$, $t_1 = r_1 + \frac{1}{2}K_6 w_1^2 - K_6 w_2^2$, $t_0 = r_0$ and

$$M_{ij} = \begin{bmatrix} 2 - \epsilon/2 & \epsilon/2 \\ 0 & 2 \end{bmatrix}. \tag{20}$$

M_{ij} has eigenvalues $\lambda^{(1)} = 2 - \epsilon/2 = \nu_1^{-1}$ and $\lambda^{(0)} = 2 = \nu_0^{-1}$. It is non-Hermitian with right and left eigenvectors $e_i^{(\alpha)}$ and $d_i^{(\alpha)}$ satisfying

$$\sum_j M_{ij} e_j^{(\alpha)} = \lambda^{(\alpha)} e_i^{(\alpha)} \qquad \sum_i d_i^{(\alpha)} M_{ij} = \lambda^{(\alpha)} d_j^{(\alpha)} \tag{21}$$

for $\alpha = 1, 0$, where $e_i^{(1)} = (0, 1)$, $d_i^{(1)} = (1, -1)$, $e_i^{(0)} = (1, 1)$ and $d_i^{(0)} = (0, 1)$. The scaling variables are thus

$$t^{(1)}(l) = \sum_i d_i^{(1)} t_i(l) = e^{\lambda^{(1)} l}(t_1(0) - t_0(0))$$

$$t^{(0)}(l) = \sum_i d_i^{(1)} t_i(l) = e^{\lambda^{(0)} l} t_0(0). \tag{22}$$

Therefore, quantities such as the mean square cluster size satisfy scaling equations of the form

$$S = [t^{(1)}]^{-\gamma_1} f\left(\frac{t^{(0)}}{[t^{(1)}]^\phi}\right) \tag{23}$$

where $\gamma_1 = (2 - \eta_1)\nu_1 = 4/(d - 2)$ and $\phi = \lambda^{(0)}/\lambda^{(1)} = 4/(d - 2) > 1$.

If the probability that a bond is occupied is varied at $K = K_c$ (i.e. $t_0 = 0$), S is proportional to $t_1^{-\gamma_1}$. If $t^{(1)} = 0$ (this corresponds to the line $J = \frac{1}{2}K$), $S \sim t_0^{-1}$ in agreement with previously discussed symmetry arguments requiring Ising exponents along this line. Finally, if $t_1 = \lambda t_0$ for any $0 < \lambda < \infty$, $S \sim t_0^{-1}$ since $\phi > 1$. Thus if the critical point is approached along any straight line path in the $t_1 - t_0$ plane, Ising-like exponents will be seen.

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