Chapter 6

Clusters and Percolation

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6.1 Introduction

In this chapter we continue our investigation of nucleation near the spinodal. We will begin by discussing the solution to the Euler-Lagrange equation in $d = 1$ and then discuss what the Langer formulation tells us about the early stage of growth of the critical droplet. Finally we discuss the structure of the spinodal droplet, a discussion that requires a digression into percolation theory.

6.2 Spinodal nucleation in one dimension

To obtain the nucleation rate and the critical droplet profile, we need to solve Eq. (5.38). This equation is very difficult to solve and has been done only numerically in $d \geq 2$. However, in $d = 1$ Eq. (5.38) can be solved exactly. The reason is that the term $[(d-1)/r]d\psi(r)/dr$ vanishes in $d = 1$ and Eq. (5.38) becomes

$$-\frac{d^2\psi(r)}{dr^2} + 4\sqrt{3}|\epsilon^{1/4}(\Delta h)^{1/2}\psi(r) - 18|\epsilon^{1/2}\,\psi^2(r) = 0. \tag{6.1}$$

The solution to Eq. (6.1) can be seen by substitution to be

$$\psi(x) = \frac{(\Delta h)^{1/2}}{\sqrt{3}|\epsilon|^{1/2}} \cosh^{-2} \frac{3^{1/4}|\epsilon|^{1/8}x}{R\,(\Delta h)^{-1/4}}, \tag{6.2}$$

where x is the one-dimensional unscaled position variable. This solution for $\psi(x)$ goes to zero as $x \to \infty$ because we have defined the order parameter in Eq. (5.19) to be zero at the metastable minimum. As expected from the scaling argument in Chapter 5, the critical droplet has an amplitude proportional to $(\Delta h)^{1/2}$ and a radius proportional to $R(\Delta h)^{-1/4}$

If we substitute the solution Eq. (6.2) into Eq. (5.20), we obtain the nucleation rate as

$$J = \lambda_s \exp[-\beta R^d (\Delta h)^{3/2} \Gamma], \tag{6.3}$$

where

$$\Gamma = \int \Big[\big[\nabla \psi'(r)\big]^2 + 2\sqrt{3}|\epsilon|^{1/4} \psi'^2(r) - 6|\epsilon|^{1/2} \psi'^3 \Big] d\vec{r}, \tag{6.4}$$

and ψ' is defined in Eqs. (5.39) and (6.2). The integral in Eq. (6.4) converges because $\cosh r$ diverges exponentially as $r \to \infty$. Moreover, we are using the scaled length variable in Eq. (6.4) so that the integrand can be considered a constant up to $r \sim (\Delta h)^{-1/4}$. These considerations imply that

$$\Gamma = C(\Delta h)^{-d/4}, \tag{6.5}$$

where C is a constant. The nucleation rate is in the form predicted in Eq. (5.40).

6.3 Early stage growth

Before considering the structure of the critical droplet, we can use the tools developed so far to obtain some information about the initial growth of the droplets. We have found the critical droplet profile by considering the solution of the Euler-Lagrange equation (5.38). As mentioned, this solution specifies a saddle point. The critical droplet is the configuration in physical space that sits on top of the saddle point in function space. It is reasonable to assume that the initial growth of the droplet corresponds to a rolling off the hill of the saddle point in the direction of the path of steepest descent [Langer 1967]. To find this path, we need to look at the Gaussian form obtained by examining small fluctuations in the LGW free energy about the saddle point. We did such a procedure in Chapter 4 when we considered the Gaussian fluctuations about stable and metastable equilibrium. Now we need the fluctuations about the saddle point associated with the critical droplet.

In analogy with the discussion following Eq. (4.11), the LGW Hamiltonian can be written in the neighborhood of the saddle point as

$$H(\psi + \eta) \approx H(\psi) + \int \big[-\eta(\vec{r})\, \nabla^2 \eta(\vec{r}) + 4\sqrt{3}|\epsilon|^{1/4} \eta^2(\vec{r}) - 36|\epsilon|^{1/2} \psi(r)\, \eta^2(\vec{r}) \big] d\vec{r} \tag{6.6}$$

where $\psi(r)$ is the solution of Eq. (5.38). To find the path of steepest descent, we need to diagonalize the Gaussian form in Eq. (6.6). Hence, we must solve the following Schrödinger-like equation in d dimensions:

$$-\nabla^2\eta(\vec{r}) + 4\sqrt{3}|\epsilon|^{1/4}(\Delta h)^{1/2}\eta(\vec{r}) - 36|\epsilon|^{1/2}\psi(r)\eta(\vec{r}) = \lambda\eta(\vec{r}). \tag{6.7}$$

For the path of steepest descent, we are interested in the negative eigenvalue that gives a non-convergent contribution to the Gaussian integral about the saddle point. The positive eigenvalues are needed as well to calculate the static prefactor λ_s. They correspond to modes of the droplet that are stable, for example, small surface deformations. The eigenvector corresponding to the negative eigenvalue tells us how the droplet grows initially as it moves away from the top of the saddle point.

For $d = 1$ and $\psi(r)$ given by Eq. (6.2) (with $r = x/R$), the solution to Eq. (6.7) is [Unger and Klein 1984]

$$\eta(x) = \cosh^{-3}[\frac{3^{1/4}|\epsilon|^{1/8}x}{R(\Delta h)^{-1/4}}]. \tag{6.8}$$

Note that the eigenvector is centered at $x = 0$, that is, at the center of the droplet. The analogy with quantum mechanics is helpful. Equation (6.7) with $\psi(r)$ given by Eq. (6.2) is of the form of a time-independent Schrödinger equation with the potential

$$4\sqrt{3}|\epsilon|^{1/2}(\Delta h)^{1/2} - 36|\epsilon|^{1/2}\psi(r). \tag{6.9}$$

The form of this potential is that of a shallow well which rises to the value $4\sqrt{3}|\epsilon|^{1/2}(\Delta h)^{1/2}$ as $r \to \infty$. The negative eigenvalue and its corresponding eigenvector describe the bound state in this picture. With this analogy in mind let us return briefly to the classical nucleation problem near the coexistence curve.

The same considerations we discussed for the spinodal case apply in the classical regime. Hence the initial growth of the critical droplet is described by the eigenvector with negative eigenvalue of the equation

$$-\nabla^2\eta(r) - 2|\epsilon|\eta(r) + 6|\epsilon|\tanh^2\left[\sqrt{2}|\epsilon|^{1/2}(r - r_0)\right]\eta(r) = \lambda\eta(r). \tag{6.10}$$

From the Schrödinger equation analogy we see that the negative eigenvalue and eigenvector describe the bound state of the potential

$$6|\epsilon|\tanh^2\left[\sqrt{2}|\epsilon|^{1/2}(r - r_0)\right] - 2|\epsilon|. \tag{6.11}$$

which is a shallow well that approaches the constant $4|\epsilon|$ as $(r - r_0) \to \infty$. The growth mode associated with the negative eigenvalue is the bound state centered at $r = r_0$, that is, at the surface of the critical droplet.

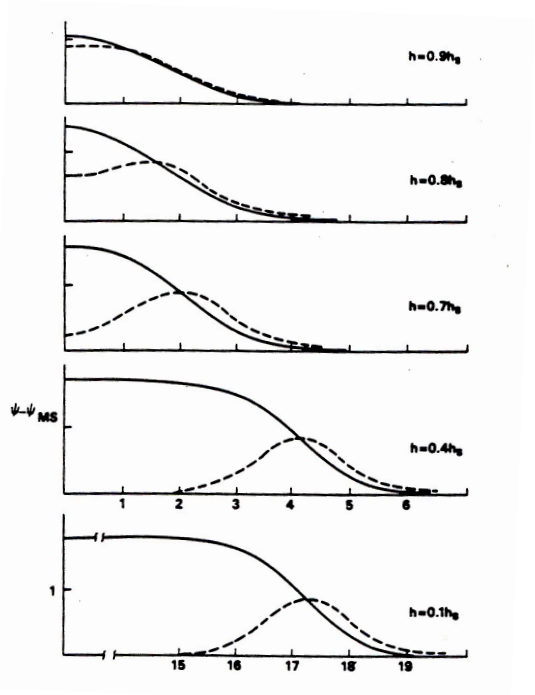

Figure 6.1: Plot of the critical droplet (solid line) and eigenvector or growth mode profiles (dashed line) obtained from the solution of the Euler-Lagrange and Schrödinger equations in $d = 3$.

The interpretation of these two results is that in the classical case where the droplets are compact objects, the initial growth takes place by particles or spins attaching themselves to the surface of the droplet. In spinodal nucleation, where the critical droplets are diffuse objects, the initial growth, which occurs in the center of the droplet, is a "filling in" or "compactifying" of the droplet. We will discuss computer simulation results of Ising models that support this point shortly.

The solutions for the eigenvectors and critical droplet profiles of the "Schrödinger" and Euler-Lagrange equations have been obtained numerically in $d = 3$ [Unger and Klein 1985]. These profiles, plotted in Fig. 6.1, confirm the results we obtained by the Schrödinger analogy. Note that the critical droplet and eigenvector vary continuously from the classical picture at $h = 0.1h_s$ to the ramified picture at $h = 0.9h_s$. An interesting interpretation [Unger and Klein 1985] of this evolution follows from noting that the eigenvector in Fig. 6.1 has a single maximum. At the maximum, $d^2\eta(x)/dx^2 < 0$ and $d\eta(x)/dx = 0$. Hence, the term $-\nabla^2\eta(x)$ is greater than 0 at the maximum of the eigenvector in Eqs. (6.7) and (6.10).

If there is an eigenvector with a negative eigenvalue in either Eqs. (6.7) or (6.9), the "Schrödinger potentials" in Eqs. (6.9) and (6.11) must be negative at the points corresponding to the maximum of the eigenvectors. This property clearly holds in the classical and the spinodal case as can be seen from Eqs. (6.9) and (6.11) where the eigenvector maxima are at $r = 0$ and $r = r_0$ respectively.

In addition, the left-hand side of Eqs. (6.7) and (6.10) are the second functional derivative of the LGW Hamiltonian evaluated at the critical droplet. Because $\psi(r)$ and $\phi(r)$ are solutions of their respective Euler-Lagrange equations, these second derivatives are essentially the second derivatives of a local free energy. The conclusion is that the maximum area of growth, that is, the maximum of the eigenvector, corresponds to a point at which the second functional derivative of the local free energy is negative. This is similar to the case of spinodal decomposition or continuous ordering discussed in Chapter 2 in which the second functional derivative of the Landau-Ginsburg free energy is negative everywhere in the system. The negative second derivative in the continuous ordering and spinodal decomposition examples was found to denote instability and the same must be true here. The conclusion is that the driving force for early growth is an instability in the droplet. Moreover the instability is confined to $r \approx r_0$ in the classical case, but the entire droplet for $r < \xi$ in spinodal nucleation. In a sense the region in which the droplet is unstable is the "surface," that is, the entire droplet near the spinodal.

6.4 Percolation: Fundamentals

Percolation is concerned with the study of clusters [Stauffer 1979]. To define a percolation model we must specify

1. the objects associated with the clustering properties we are studying;
2. how these objects are distributed, and
3. what is meant by connected.

Percolation theory is concerned with the properties of the resultant clusters.

As an example, consider a lattice whose vertices are either occupied randomly with probability p or are empty with probability $q = 1 - p$. The objects we are considering are occupied sites, which are distributed at random. We define as connected two nearest neighbor sites that are occupied. These properties define the random site percolation model.

We define an s site cluster as s mutually connected sites that are not connected to any other sites outside the s site cluster. In Fig. 6.2 there is a five site cluster and a two site cluster.

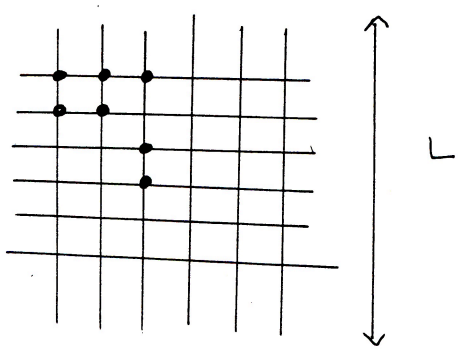

Figure 6.2: Lattice of linear dimension L with one 5 site cluster and one 2 site cluster.

Our interest is in the properties of the clusters. The first point to consider is the following: Suppose we have a large number of finite square lattices such as the one in Fig. 6.2 of linear dimension L. On each lattice we occupy sites with probability p. Beginning at $p = 0$ we raise the probability of occupying a site until we obtain a cluster that spans the lattice and note the value of p at which each lattice is spanned. By a cluster that spans we mean a cluster that connects one side of the lattice to the opposite side. The values at which the individual lattices are spanned vary widely for small L. As L increases the variation in the spanning value of p decreases until all (except for a set of measure zero) lattices span at the same value $p = p_c$ as $L \to \infty$. The value $p = p_c$ is called the percolation threshold, which depends on the details of the lattice. For example in $d = 2$ $p_c = 1/2$ for a triangular lattice and $p_c \approx 0.5927$ for a square lattice [Stauffer 1979].

At $p = p_c$ the spanning cluster is called the incipient infinite cluster. For $p > p_c$ there is also a spanning cluster that we refer to as the infinite cluster. The incipient infinite cluster and the infinite cluster have very different structure as we will see.

If we plot the probability that an *occupied* site belongs to the infinite or spanning cluster $P(p)$ we find a curve such as shown in Fig. 6.3.

The value of $P(p)$ is zero for $p < p_c$ as it must be. In addition, we find that not only does $P(p)$ go to zero continuously, it vanishes as a power of $\Delta p \equiv (p - p_c)/p_c$. We define the critical exponent β_p by the relation

$$P(p) \propto (\Delta p)^{\beta_p}. \tag{6.12}$$

We can also define the mean size of the *finite* clusters χ_p as

$$\chi_p \propto \sum_s{}' s^2 n_s(p), \tag{6.13}$$

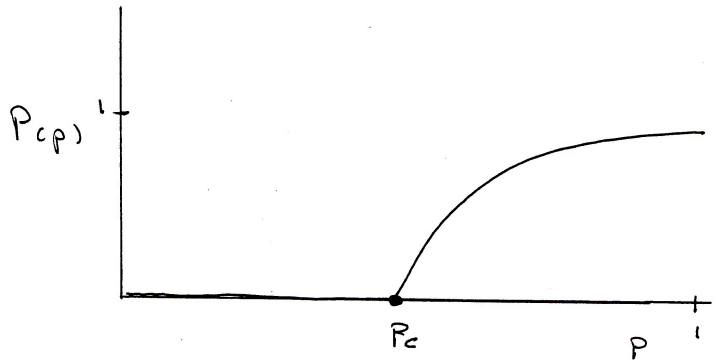

Figure 6.3: The probability that an occupied site belongs to the spanning cluster as a function of p.

where $n_s(p)$ is the mean number of clusters of s occupied sites per lattice site, and the prime indicates that the sum is to be performed only over the finite clusters. The prime is only meaningful if $p > p_c$. Figure 6.4 is a schematic plot of χ_p versus p. At $p = p_c$, χ_p diverges with a power law. We define the critical exponent γ_p by the relation

$$\chi_p \sim (\Delta p)^{-\gamma_p}. \tag{6.14}$$

We can also measure the mean diameter of the finite clusters ξ_p that will diverges with a power law at $p = p_c$. As in the case of χ_p we can define the exponent ν_p by the relation

$$\xi_p \sim (\Delta p)^{-\nu_p}. \tag{6.15}$$

Finally we can define the mean number of finite clusters as

$$G(p) = \sum_s{}' n_s(p). \tag{6.16}$$

This quantity is singular at $p = p_c$. If we call $G_s(p)$ the singular part of $G(p)$, we can define the exponent α_p through the relation

$$G_s(p) \sim (\Delta p)^{2-\alpha_p}. \tag{6.17}$$

As their definitions might suggest, the singularities in percolation quantities have a strong resemblance to the analogous quantities in thermal phase transitions. For example, numerical simulations and exact results in mean-field models and in $d = 1$ show that the percolation exponents we have defined obey the scaling relation

$$\alpha_p + 2\beta_p + \gamma_p = 2, \tag{6.18}$$

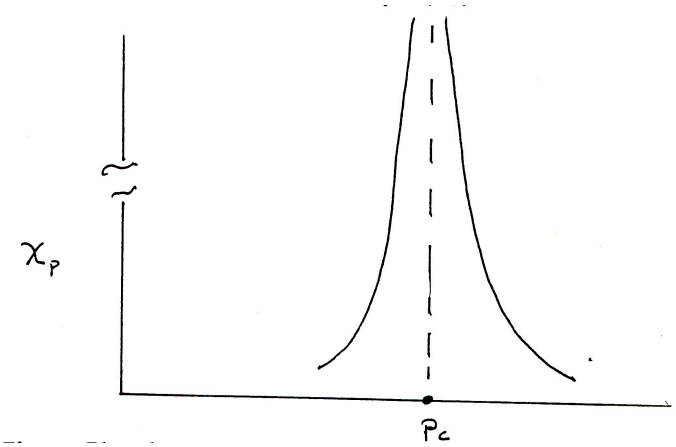

Figure 6.4: Plot of χ_p versus p.

just as the thermal exponents. Moreover, the exponents fall into broad universality classes so that, for example, the exponents do not depend on lattice type, but do depend on the spatial dimension.

To make the analogy with thermal phenomena even stronger, we can define a parameter $\tilde{h}$, usually referred to as the ghost field, and the generating function

$$G(p,\tilde{h}) = \sum_s{}' n_s(p) e^{-\tilde{h}s}. \tag{6.19}$$

The singular part of three of the four quantities we have defined, $\chi_p, P(p)$ and $G_s(p)$, can be related to $G(p,\tilde{h})$. If we denote the singular part of $P(p)$ as $P_s(p)$, then

$$P_s(p) \propto \frac{\partial G(p,\tilde{h})}{\partial \tilde{h}}\Big|_{\tilde{h}=0} \tag{6.20}$$

If χ_{ps} is the singular part of χ_p, then

$$\chi_{ps} \propto \frac{\partial^2 G(p,\tilde{h})}{\partial \tilde{h}^2}\Big|_{\tilde{h}=0}. \tag{6.21}$$

From these relations and their comparison with the relation between the derivatives of the thermal free energy with respect to the magnetic field and the analogous thermal quantities such as χ_T, we see that $G(p,\tilde{h})$ plays the role of the free energy and $\tilde{h}$ the magnetic field. For the exact relations between the percolation quantities and $G(p,\tilde{h})$ see Reynolds et al. 1977.

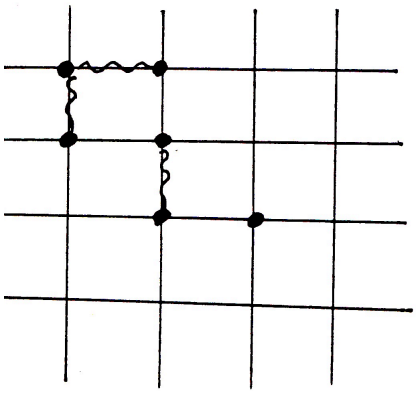

Figure 6.5: Occupied bonds are denoted by wavy lines. There is one $s = 3$ site, one $s = 2$ site and one $s = 1$ site cluster shown.

At $\tilde{h} = 0$, $G(p) = \sum_s' n_s(p)$ which is the mean number of clusters per site. If we restrict our considerations to $\tilde{h} > 0$, we can interpret $e^{-\tilde{h}}$ as the probability that a given site is not connected to a ghost site. The ghost site is a single "super site" which can be attached to all of the sites in the lattice with a probability $1 - e^{-\tilde{h}}$. Consequently, $e^{-\tilde{h}s}$ is the probability that an s site cluster is not attached to the ghost site.

If $\tilde{h} \neq 0$, the ghost site is attached to an infinite number of sites in the limit $L \to \infty$ and hence is a part of an infinite cluster. Therefore $G(p, \tilde{h})$ is the mean number of finite clusters even if $\tilde{h} \neq 0$.

These considerations can be generalized to other percolation models. For example, we can have the same lattice as in Fig. 6.2, but all sites are occupied and the bonds between sites can be occupied or empty. If the bond occupation is distributed at random with a probability p and we define as connected two nearest neighbor sites that have an occupied bond between them, we have the random bond percolation model. All of our previous considerations still apply. Moreover, the values of the critical exponents are the same as for site percolation but as might be expected, the values of the percolation thresholds are different.

Another variation of these percolation models is to distribute occupied sites randomly with probability p_s *and* occupied bonds randomly with a probability p_b. Two nearest neighbor sites are connected if they are both occupied and have an occupied bond between them (see Fig. 6.5).

As with the random bond percolation model, the critical exponents are the same as in the site model however, the percolation threshold is expanded from a point ($p = p_c$) to a line in the $\tilde{h} = 0$, p_b, p_s plane (see Fig. 6.6).

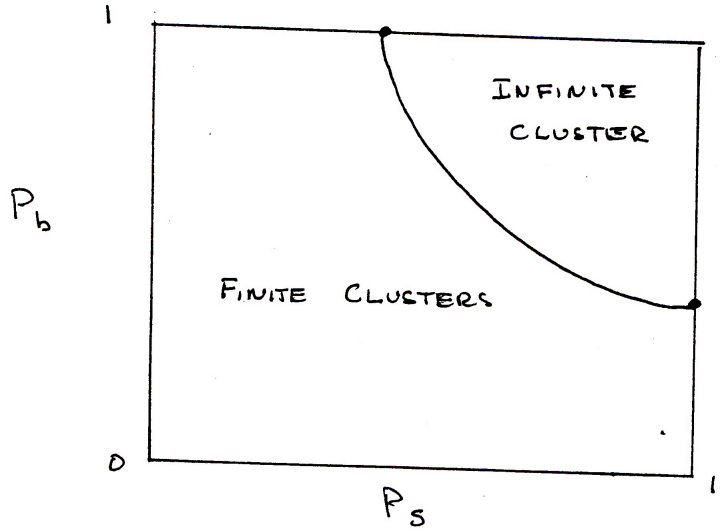

Figure 6.6: The percolation threshold in the $\tilde{h} = 0$, p_b, p_s plane. At $p_s = 1$ ($p_b = 1$) the threshold is at the bond (site) value.

A very useful class of models is generated by realizing that the random site model can be obtained from the Ising model at temperature $T = \infty$. We can designate a down spin as an occupied site and an up spin as an empty site. Because $T = \infty$ the spins are distributed at random with a probability

$$p = \rho = \frac{1 - m}{2} = \frac{1 - \tanh(\tilde{h})}{2}, \tag{6.22}$$

where m is the magnetization per spin. The ghost field $\tilde{h}$ is used in the same manner as discussed previously. We can easily add random bonds to this model in the same way we did before to recover the random site-random bond model.

The most interesting modification we can make to these models from the point of view of the kinetics of phase transitions is to maintain the identification of a down spin with an occupied site and an up spin with an empty but to distribute the spins according to the Ising Boltzmann factor $e^{-\beta H}$ where the Ising Hamiltonian $-\beta H$ is given in Eq. (1.4). We then measure percolation properties of these spins. This model, with nearest neighbor occupied sites connected, is called the correlated site percolation model. We can also introduce random bonds as we did before so that nearest neighbor occupied sites are connected only if there is an occupied bond between them. We call this model correlated site-random bond percolation. The latter model will play an important role in the understanding of nucleation near the spinodal. For the moment, however, let us return to the correlated site problem ($p_b = 1$).

Suppose we start the system at $T = 0$ with all spins up (sites empty). We now begin to raise the temperature, which results in more spins becoming down (occupied sites). At $T = T_c$, the critical temperature of the Ising model, the system has an infinite correlation length ξ. What, if anything, does the critical point have to do with the percolation problem? In can be shown rigorously [Coniglio et al. 1977] in $d = 2$ that T_c corresponds also to the percolation threshold.

Moreover, renormalization group arguments [Klein et al. 1978, Coniglio and Klein 1980] indicate that $\nu_p = \nu$, where ν is the Ising correlation length exponent. What about other critical exponents? Numerical measurements [Sykes and Gaunt 1976] of γ_p as the critical point is approached indicate that $\gamma_p > \gamma$, where γ is the Ising susceptibility exponent.

Consider the same problem in $d = 3$. We start the system at $T = 0$ with all spins up, increase the temperature and note the percolation threshold. It has been found numerically [Müller-Krumbhaar 1974] that in three dimensions the percolation transition occurs at T_p and $T_p < T_c$.

The two-dimensional results that $T_p = T_c$ and $\nu_p = \nu$ were encouraging because if all the critical exponents and the transition temperature were the same, then it would be a strong indication that the correlated site percolation clusters were describing the Ising fluctuations. The results that $\gamma_p > \gamma$ in $d = 2$ and $T_p < T_c$ in $d = 3$ show that these clusters are not the right ones. However, these two results indicate that we might be able to improve the situation by using the correlated site-random bond model. The reason that this model might work is that these results suggest that the correlated site clusters are too big, that is, they have too many spins. If we introduce $p_b \neq 1$, we need more spins to percolate (see Fig. 6.6) and hence push the percolation threshold in $d = 3$ to a higher value of T. The $d = 2$ case is a bit more subtle and requires more background discussion.

We can define the fractal dimension d_f of the incipient infinite cluster by asking how the volume or mass m scales with the connectedness length ξ_p

$$m \sim \xi_p^{d_f}. \tag{6.23}$$

We can obtain the incipient infinite cluster by starting at $p > p_c$ and approaching p_c from above. The probability that a site belongs to the infinite cluster is proportional to $P(p)$ so that the mass of the infinite cluster close to p_c is proportional to

$$m \sim P(p)\xi_p^d. \tag{6.24}$$

However,

$$P(p) \propto (\Delta p)^{\beta_p} \propto \xi_p^{\beta_p/\nu_p}, \tag{6.25}$$

so that

$$m \sim \xi_p^{d-\beta_p/\nu_p} \tag{6.26}$$

From two exponent scaling at critical points [Reynolds et al. 1977, Coniglio et al. 1977]

$$d - \frac{\beta_p}{\nu_p} = d - \frac{d - y_{\tilde{h}}}{y_p} y_p = y_{\tilde{h}}, \tag{6.27}$$

where $y_{\tilde{h}}$ is the scaling power associated with the ghost field and y_p is the scaling power associated with (Δp).

These considerations point out one major difference between the infinite and incipient infinite clusters. For the infinite cluster $P(p)$ does not vanish. We can still use Eq. (6.24) to define the fractal dimension of the infinite cluster and because $P(p) > 0$, $d_f = d$.

Lets return to the critical point and assume that there exists a percolation model whose critical exponents are the same as the Ising model. The fractal dimension of the clusters at the percolation threshold, and by assumption at the Ising critical point, is y_h, the scaling power associated with the Ising magnetic field. Moreover, for this assumed model $y_p = y_T$, that is, the percolation scaling power associated with the variable Δp is the same as that associated with the thermal variable ΔT.

We again use the two exponent scaling relations [Reynolds et al. 1977, Coniglio et al. 1977] and obtain

$$\gamma_p = \gamma = \frac{2y_h - d}{y_T}. \tag{6.28}$$

For the correlated site percolation model where we also have $y_p = y_T$ we know that $\gamma_p > \gamma$. This relation implies with Eq. (6.28) that $y_{\tilde{h}}$ for the correlated site percolation model is greater than y_h for the Ising model and our postulated percolation model which we have assumed is equivalent to the Ising model. From Eq. (6.27) we would then conclude that the correlated-site clusters have a fractal dimension which is larger than the postulated model that we still must find. Thus the correlated-site model has clusters which are too big and bond dilution might work.

To find the right model we need more powerful tools, which we develop in the next chapter.

Suggestions for Further Reading

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