

1 Elements of percolation theory: on the way to gels

Percolation addresses the purely geometric problem of the connectivity of a system of points arranged in space according to a predefined distribution. In the simplest case points are distributed on a lattice (in d dimensions). Given the points and their distribution, percolation theory requires a definition of connection between adjacent lattice points. The term site-percolation is used when two occupied adjacent points are defined as connected, bond-percolation when a link must exist between the two points.

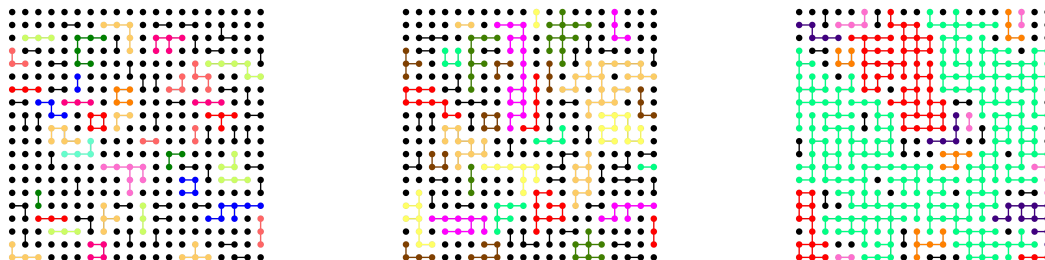


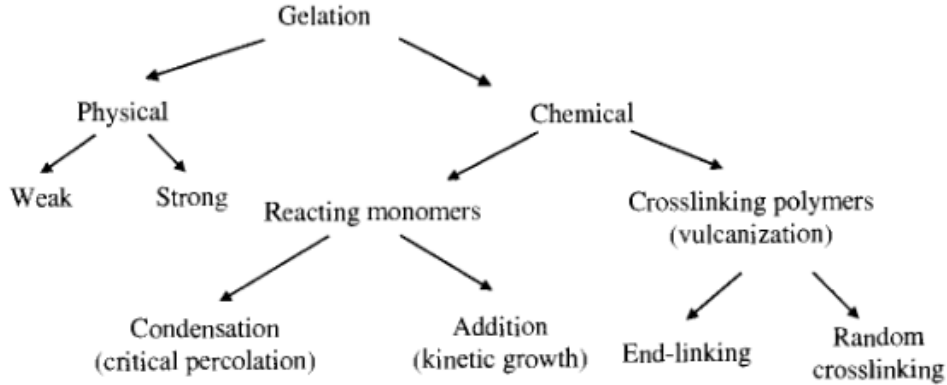
Figure 1: Example of random-bond percolation on a square lattice for 3 different values of the probability of existence of a bond. The different clusters are indicated with different colours.

One of the main questions which the theory poses is the evaluation of the value of the control parameter (the density of sites in site-percolation or the bond-percolation probability) for which the system reaches a percolating configuration, that is one configuration for which a cluster spanning the entire system emerges. Equally important is to predict the behavior of observables affected by connectivity properties in the vicinity of the so-called percolation threshold. Figure 1 shows an example of a bond-percolation in two dimensions for three different values of the bond probability p . Adjacent sites connected by links and partitioned into clusters. At low p the clusters are small and separated. At the critical value $p_c = 1/2$, an infinite cluster is observed even if with tenuous connections (i.e. such that it is enough to eliminate a few links to disconnect the cluster in several smaller clusters).

Why should we take care of percolation? There are numerous phenomena in physics that require concepts of connectivity. Often, to identify the conditions for which an infinite "cluster" that transmits information on macroscopic dimensions exists is quite important. Let's think, for example, of electrical conductivity in a disordered system, to the elasticity in a two-component system with different mechanical properties, to the spread on disordered systems, for example of diseases, or the propagation of forest fires.

The percolative approach is of particular relevance in the study of polymeric and colloidal systems, especially for the study of the gel state. Polymeric systems with molecules that form chemical cross-links constitute one of the systems in which the formation of a network permanent depends on the functionality of the polymers and the number of bonds. The gels are divided into two broad categories: chemical gels and physical gels. In the former the bonds are the result of a chemical reaction and therefore the energy of the bond, much higher than kT , guarantees the stability of the bond itself. In physical gels, a temperature increase even modest can melt the gel, since the energy of the bond is of the order of kT .

Random branching and gelation



Near the percolation threshold, as in critical phenomena near the critical point, many properties connected to connectivity show scaling laws (power law), that is they show the absence of a characteristic length. The characterization of scale exponents allows us to establish the class of universality of the percolation phenomenon, in close analogy with thermal phenomena.

To start familiarising with percolation, let us first examine the solvable cases of site and bond-percolation in one dimension, which will allow us to define the quantities used in the description and their inter-relations.

1.1 1-d site percolation

In this problem, the external control parameter is the probability p of occupation of a site of an infinite chain. This one-dimensional model is clearly pathological, because the percolation threshold requires that all sites are present, ie $p_c = 1$. So, in this model, we can only study the behavior for $p < p_c$.

The random occupation of the sites, with probability p creates a distribution of clusters of different size. Let's call N_s the number of clusters of size s found in the system and let's try to quantify this distribution.

A cluster of size s requires s occupied sites and 2 unoccupied ones at the end. Then, a part from a still unknown normalization numerical factor

$$N_s = A(1 - p)^2 p^s$$

To calculate the prefactor A , we can consider that if we sum over all clusters, the fraction of occupied sites must be again p . In other words, remembering that a cluster of size s is composed by s occupied sites

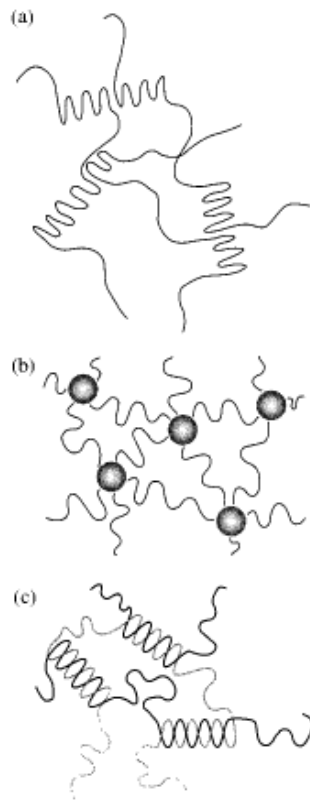


Fig. 6.3
Examples of strong physical gels
with crosslinks that are: (a) lamellar
microcrystals; (b) glassy nodules;
(c) double helices.

$$p = \frac{\sum_{s=1}^{\infty} sN_s}{N}$$

where N is the total number of lattice sites. Let's perform the sum

$$Np = \sum_{s=1}^{\infty} sN_s = A \sum_{s=1}^{\infty} sp^s(1-p)^2 = A(1-p)^2 \sum_{s=1}^{\infty} sp^s = A(1-p)^2 \sum_{s=1}^{\infty} p \frac{d}{dp} p^s = Ap(1-p)^2 \frac{d}{dp} \sum_{s=1}^{\infty} p^s \quad (1)$$

$$= Ap(1-p)^2 \frac{d}{dp} \frac{p}{1-p} = Ap(1-p)^2 \frac{1}{(1-p)^2} = Ap \quad (2)$$

which shows that $A = N$. The previous calculation also shows that the first moment of the cluster size distribution is trivial $\sum_{s=1}^{\infty} sN_s = Np$. It is more interesting to study the behavior of the second moment of the distribution N_s , called **mean cluster size** S and defined as

$$S = \frac{\sum_{s=1}^{\infty} s^2 N_s}{\sum_{s=1}^{\infty} s N_s} = \frac{\sum_{s=1}^{\infty} s^2 N_s}{Np} \quad (3)$$

Evaluating S

$$NpS = \sum_{s=1}^{\infty} s^2 N_s = N(1-p)^2 \sum_{s=1}^{\infty} s^2 p^s = N(1-p)^2 \left\{ p^2 \frac{d^2}{dp^2} \sum_{s=1}^{\infty} p^s + p \frac{d}{dp} \sum_{s=1}^{\infty} p^s \right\} = \quad (4)$$

$$= N(1-p)^2 \left\{ p^2 \frac{d^2}{dp^2} \frac{p}{1-p} + Np \frac{d}{dp} \frac{p}{1-p} \right\} \quad (5)$$

and knowing that

$$\frac{d}{dp} \frac{p}{1-p} = \frac{1}{(1-p)^2} \quad (6)$$

$$\frac{d^2}{dp^2} \frac{p}{1-p} = \frac{d}{dp} \frac{1}{(1-p)^2} = \frac{2}{(1-p)^3} \quad (7)$$

one finds (simplifying N on both sides)

$$pS = (1-p)^2 \left\{ \frac{2}{(1-p)^3} + \frac{1}{(1-p)^2} \right\} = \frac{p(1+p)}{1-p} \quad (8)$$

from which

$$S = \frac{1+p}{1-p} \quad (9)$$

The mean cluster size diverges to the percolative transition $p = 1$ with a power law with an exponent -1 .

Let us now examine the probability $P_2(r)$ that a randomly chosen site is connected to a site distant r on the right side. This probability is given by

$$P_2(r) = p^r \quad (10)$$

In fact connectivity is guaranteed if the r following sites are occupied. We can rewrite the same probability as

$$P_2(r) = p^r = e^{-r/\xi} \quad (11)$$

where we have defined the connectivity length ξ as

$$\xi = -\frac{1}{\ln p} \quad (12)$$

Close to the transition, $p \rightarrow p_c \equiv 1$, and hence we can write

$$\ln p = \ln p_c + (p - p_c) \quad (13)$$

and close to p_c

$$\ln p = \ln 1 + (p - p_c) \approx -|p - p_c| \quad (14)$$

and

$$\xi \sim \frac{1}{|p - p_c|} \quad (15)$$

Therefore the connectivity length diverges to the transition also like a power law.

S and $P_2(r)$ are linked by an integral relation. In fact, if we sum $P_2(r)$, where the factor 2 account for positive and negative r

$$\sum_{-\infty}^{\infty} P_2(r) = 1 + 2 \sum_{r=1}^{\infty} p^r = 1 + 2 \frac{p}{1-p} = \frac{1+p}{1-p} = S \quad (16)$$

Finally, let us exam an alternative way to write N_s for $|p - p_c| \ll 1$.

$$N_s = N(1-p)^2 p^s = N(1-p)^2 e^{s \ln(p)} = N(p_c - p)^2 e^{-s(p-p_c)} \quad (17)$$

and defining a variable $x = s(p - p_c)$ we can write

$$N_s = N \frac{x e^{-x}}{s^2} = s^{-2} N x e^{-x} = s^{-2} f(x) \quad (18)$$

which tells us that N_s near the percolation can be expressed as a power law for a scale function $f(x)$ of the variable x . We note that a graph of $s^2 N_s$ vs x would give a complete "collapse" (date collapse) of all curves, regardless of the value of $p - p_c$.

In summary, in the vicinity of the critical point in one dimension, the percolation properties follows power laws and these laws are summarized in the following table.

Table 1: Results 1-d percolation

$$\left| \begin{array}{l} S \sim |p - p_c|^{-1} \\ \xi \sim |p - p_c|^{-1} \\ n_s \sim s^{-2} f[s|p - p_c|] \\ P_\infty = 0 \end{array} \right|$$

1.1.1 bi-functional molecules: a bond-percolation model

Next we move off-lattice, retaining the one-dimensional aspect of the problem. Suppose we have a molecule with two reactive groups, which we call A and B and suppose that reactive group A links only to reactive group B.

We call p the fraction of groups that have reacted $N_{reacted}$ over the total number of A groups, equal to the number N of molecules). Thus in this case we can define $p = N_{reacted}/N$. We can immediately write that the total number of clusters $N_{clusters}$ is

$$N_{clusters} = N - N_{reacted} = N - Np = N(1 - p)$$

since each cluster has only one group A that has not reacted. Therefore the average length of the clusters will be

$$\frac{N}{N_{clusters}} = \frac{1}{1 - p}$$

The number of clusters composed of n monomers, (with $n - 1$ reacted sites) will be

$$N_n = N(1 - p)^2 p^{n-1}$$

where the normalization is chosen such that

$$\begin{aligned} \sum_{n=1}^{\infty} nN_n &= \sum_{n=1}^{\infty} nN(1-p)^2 p^{n-1} = N(1-p)^2 \sum_{n=1}^{\infty} \frac{d}{dp} p^n = \\ N(1-p)^2 \frac{d}{dp} \sum_{n=1}^{\infty} p^n &= N(1-p)^2 \frac{d}{dp} \frac{p}{1-p} = N(1-p)^2 \frac{1-p+p}{(1-p)^2} = N \end{aligned}$$

1.2 A maximum-entropy approach to the same problem

It is quite instructive to predict the cluster size distribution for a system of N bifunctional particles dispersed in a volume V , knowing that these particles have formed exactly P bonds. For particles with valence two, the possible clusters are chains of variable length n . Then, assuming that the different chains do not interact, the configurational part of the partition function of the system can be written as the product of the partition functions of the individual clusters Q_n , each of them normalised by an $N_n!$ term which accounts for permutations of identical clusters

$$Q = e^{-\beta P \mathcal{F}_b} \prod_n \frac{Q_n^{N_n}}{N_n!} \quad \text{with} \quad Q_n = \frac{\Omega_n}{n!} V,$$

where \mathcal{F}_b is the free energy associated to the existence of one bonds (and being multiplied by P , $P\mathcal{F}_b$ is the free energy associated to the existence of P bonds), Ω_n indicates the number of ways n distinct particles, each with two distinct reactive sites A and B and only AB bonds, can be joined into a chain of length n . The volume term V , expressed in units of the cube of the thermal length, accounts for the cluster center of mass entropy. Considering that the first patch in the chain can be selected in n ways, that the bonded patch of the second particle can be selected in $(n-1)$ ways and so on, one finds $\Omega_n = n!$. As a result,

$$Q = e^{-\beta P \mathcal{F}_b} \prod_n V^{N_n} / N_n!. \quad (19)$$

Apart from the constant contribution associated to the presence of P bonds, $e^{-\beta P \mathcal{F}_b}$, the remaining free-energy contribution ($-k_B T \ln Q$) is purely entropic and coincides with the one of an ideal gas of chains distributed according to N_n ,

$$\frac{S}{k_B} = \sum_{n=1}^{\infty} N_n \left\{ 1 - \ln \frac{N_n}{V} \right\}. \quad (20)$$

The solution for the most probable distribution of chain lengths N_n can now be calculated by requiring that entropy assumes the largest possible value, but satisfying the two constraints in the problem: the conservation of the number of particles ($\sum_{n=1}^{\infty} nN_n = N$) and the total number of bonds. Since each chain of length n has $n-1$ bonds, the constraint on the number of bonds can be formulated as $\sum_{n=1}^{\infty} (n-1)N_n = P$.

Defining $\ln \alpha$ and $\ln \beta$ as the Lagrange multipliers associated to the two constraints, the maximization of the entropy S with respect to N_n , including the contribution arising from the Lagrange multipliers, gives

$$\frac{dS}{dN_n} = \left(1 - \ln \frac{N_n}{V}\right) - 1 + n \ln \alpha + (n-1) \ln \beta = \ln \left[\frac{V}{N_n} \alpha^n \beta^{n-1} \right] = 0 \quad (21)$$

or equivalently

$$\frac{N_n}{V} = \alpha(\alpha\beta)^{n-1}. \quad (22)$$

Re-defining $\gamma = \alpha\beta$ for simplicity and plugging this result in the equations defining the two constraints, it is possible to calculate the exact values of α and β . Indeed

$$N = \sum n N_n = V \alpha \sum_{n=1}^{\infty} n \gamma^{n-1} = V \alpha \frac{d}{d\gamma} \sum_{n=1}^{\infty} \gamma^n = V \alpha \frac{d}{d\gamma} \frac{\gamma}{1-\gamma} = \frac{V \alpha}{(1-\gamma)^2}$$

such that

$$V \alpha = N(1-\gamma)^2$$

The second constraint is

$$P = \sum_n (n-1) N_n = N - \sum_n N_n = N - V \alpha \sum_{n=1}^{\infty} \gamma^{n-1} = N - N(1-\gamma)^2 \frac{1}{\gamma} \sum_{n=1}^{\infty} \gamma^n = N - N(1-\gamma)^2 \frac{1}{\gamma} \frac{\gamma}{1-\gamma} = N\gamma$$

In terms of fraction of formed bonds $p = P/N$, one thus finds $\alpha\beta = \gamma = p$ and $\alpha V = N(1-p^2)$, such that

$$N_n = V \alpha (\alpha\beta)^{n-1} = N(1-p^2)p^{n-1} \quad (23)$$

The equilibrium cluster size distribution N_n is thus exponential, a well known result of equilibrium polymerization. The result can also be easily interpreted as a chain with two open bonds at the ends $((1-p)^2)$ times $n-1$ bonds between the n particles (p^{n-1}).

1.3 Bond percolation sul reticolo di Bethe

Next we discuss percolation on a lattice, named Bethe lattice, in which many statistical physics problems can be analytically solved. This lattice expands over the one dimensional case, allowing for multiple connections at the lattice site, but retains the simplicity of the one-dimensional case since it neglects the possibility of loops formation.

In the Bethe lattice each site is connected with z neighbours. The absence of cyclical structures allows the analytical calculation of percolation properties. Let's start with the calculation of p_c for bond percolation. If we call p the probability of existence of a bond, the average number of nearest neighbour sites connected to the central site is $C_1 = zp$. The average number of sites of second generation connected to the central one is $C_2 = (z-1)pC_1$. In fact there are $z(z-1)$ distant sites two and to be connected one needs two bonds (p^2). The number of site at generation N will be $C_N = (z-1)pC_{N-1} = [(z-1)p]^{N-1}C_1$. Thus the number of sites after an infinite number of iterations connected to the central site is zero if $(z-1)p < 1$ and different from zero if $(z-1)p > 1$. The critical value it is therefore given by

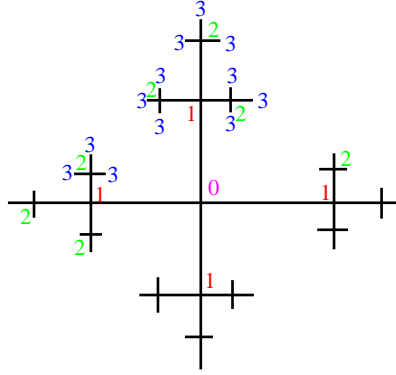


Figure 2: Bethe Lattice

$$p_c = \frac{1}{z-1} \quad (24)$$

We now estimate the fractions of particles belonging to the infinite cluster.

As a preliminary step, we calculate $Q(p)$, defined as the probability that a site is not connected to infinity through a specific branch.

If we consider an arbitrary site and a branch, the probability $Q(p)$ for that branch can be written as

$$Q(p) = (1-p) + pQ(p)^{z-1} \quad (25)$$

since the first bond (the one that starts the branch) is "empty" with probability $1-p$ and "full" with probability p . If it is full, it will not go to infinity only if all $z-1$ sub-branches are not connected.

The solution of the preceding equation gives us the dependence on p of $Q(p)$. In the analytically solvable case of $z=3$, we have

$$Q(p) = 1-p + pQ(p)^2 \quad (26)$$

which has as a solution

$$Q(p) = \frac{1 \pm (1-2p)}{2p} \quad (27)$$

The solution $Q(p) = 1$ is always valid. The other solution

$$Q(p) = \frac{1-p}{p}$$

appears only when $Q(p) < 1$ i.e. for $p > 1/2 = p_c$. So, for $p > p_c$, $1 - Q(p)$, which is the probability that an arbitrarily chosen link is connected to infinity becomes different from zero.

Let us now calculate P_∞ , the probability that a randomly chosen site belongs to the infinite cluster. Of course $P_\infty = 0$ for $p < p_c$. The site is connected to infinity if none of the branches is connected to infinity ($Q(p)^z$). Therefore

$$P_\infty = 1 - Q(p)^z \quad (28)$$

For $p < p_c$, $Q(p) = 1$ and hence $P_\infty = 0$. To study the behavior of P_∞ around p_c let's look explicitly to the case $z = 3$, for which

$$P_\infty = \left[1 - \left(\frac{1-p}{p} \right)^3 \right] \quad (29)$$

Close to p_c we can expand P_∞ in Taylor series

$$\begin{aligned} \frac{dP_\infty}{dp} &= \left[-3 \left(\frac{1-p}{p} \right)^2 \frac{-p-1+p}{p^2} \right] \\ P_\infty &\approx \left[3 \left(\frac{1-p}{p} \right)^2 \frac{1}{p^2} \right]_{p=p_c} (p - p_c) = 12(p - p_c) \end{aligned} \quad (30)$$

Then $P_\infty = 0$ grows with a power law around p_c with exponent $\beta = 1$, a typical mean field exponent.

Let us now examine the mean cluster size S , defined as the average size of the cluster. S indicates the average size of the cluster to which an arbitrary site belongs. We call the average size of the cluster of a branch of the Bethe lattice with T . Even for T it is possible to write one recurrence relation

$$T = p(1 + (z-1)T) + (1-p)0 \quad (31)$$

$$T = \frac{p}{1-p(z-1)} = \frac{pp_c}{p_c-p} \quad (32)$$

This expression indicates that the cluster size of an arbitrary branch has the same average size as the cluster size of each sub-branch.

To calculate S , we choose an arbitrary site and write (replacing $z = \frac{1+p_c}{p_c}$)

$$S = 1 + zT = 1 + \frac{1+p_c}{p_c} \frac{pp_c}{p_c-p} = \frac{p_c-p+p+pp_c}{p_c-p} = p_c \frac{1+p}{p_c-p} \sim (p_c-p)^{-1} \quad (33)$$

Hence, the mean cluster size diverges with a power $\gamma = -1$

Now let's take a look at the size distribution of the clusters. Here the topology of the Bethe lattice enters very clearly, because every cluster, regardless of its shape, has the same perimeter (defined as the number of links bordering the cluster, or number of empty sites bordering the cluster). This property (which is true in one dimension and in Bethe), allows you to write immediately

$$n_s = g_s p^s (1-p)^{t_s} \quad (34)$$

where t_s is the perimeter and g_s is a combinatorial term that tells in how many ways a cluster of size s can be built. Considering site percolation, the first site has z perimeters, each added site consumes a perimeter site but adds $z-1$ sites. Then $t_s = z + (s-1)(z-2) = 2 + s(z-2)$.

Since g_s is difficult to calculate, consider the relationship between $n_s(p)$ and $n_s(p_c)$

$$\frac{n_s(p)}{n_s(p_c)} = \frac{(1-p)^2}{(1-p_c)^2} \frac{[p(1-p)^{(z-2)}]^s}{[p_c(1-p_c)^{(z-2)}]^s} \quad (35)$$

If we Taylor expand $y \equiv \frac{p(1-p)^{(z-2)}}{p_c(1-p_c)^{(z-2)}}$ near p_c we find (substituting z with p_c , e.g. $z-2 = [1-p_c]/p_c$)

$$y(p_c) = 1 \quad \left. \frac{dy}{dp} \right|_{p_c} = 0 \quad \left. \frac{d^2y}{dp^2} \right|_{p_c} = \frac{1}{p_c^2(p_c-1)}$$

$$y \approx 1 + \frac{(p-p_c)^2}{2p_c^2(p_c-1)} \quad (36)$$

Then we can write

$$\frac{n_s(p)}{n_s(p_c)} \approx \left(1 + \frac{(p-p_c)^2}{2p_c^2(p_c-1)} \right)^s = e^{s \log \left(1 + \frac{(p-p_c)^2}{2p_c^2(p_c-1)} \right)} = e^{-cs} \quad (37)$$

with $c = \frac{(p-p_c)^2}{2p_c^2(p_c-1)}$

As a result, close to p_c ,

$$n_s(p) = n_s(p_c)e^{-cs} \quad (38)$$

where, we remember, $n_s(p_c)$ includes g_s . Instead of calculating (which is possible but long for Bethe) g_s , take the solution for $n_s(p_c)$ and continue from there. This solution, which for Bethe can be calculated analytically, it becomes an unsatz for all other cases. We therefore assume that

$$n_s(p_c) \sim s^{-\tau} \quad (39)$$

and hence

$$n_s(p) \sim s^{-\tau} e^{-cs} \quad (40)$$

The exponent τ can be calculated imposing consistency. Indeed, $S = \sum_s s^2 n_s$. We can write

$$S = \sum s^{2-\tau} e^{-cs} \quad (41)$$

and close to p_c where

$$S = \int_0^\infty s^{2-\tau} e^{-cs} ds \quad (42)$$

$$S = c^{\tau-3} \int_0^\infty (cs)^{2-\tau} e^{-cs} d(cs) \sim c^{\tau-3} \quad (43)$$

Since we know that $S \sim (p_c - p)^{-\gamma} \sim (p_c - p)^{-1}$ we have to conclude that $2(\tau - 3) = -1$, where 2 comes from the fact that $c \sim (p - p_c)^2$. Then we find $\tau = \frac{5}{2}$.

In summary, two exponents inherent in n_s (τ and the exponent that controls c) determine the value of γ (and, it is possible to show, also of P_∞ .)

2 The soluble Flory-Stockmayer case

In the case of particles with functionality f , where each site can interact with identical sites of distinct particles (AA bonds), assuming that they aggregate without forming closed loops, it is possible to show that the distribution of the clusters is given by

$$N_n = N(1-p)^f \frac{f(fn-n)!}{n!(fn-2n+2)!} [p(1-p)^{f-2}]^{n-1} \quad (44)$$

and that percolation is reached when $p^c = \frac{1}{f-1}$. The cluster structure at p^c is

$$N_n(p^c) = N \left(\frac{f-2}{f-1} \right)^f \frac{f(fn-n)!}{n!(fn-2n+2)!} \left[\frac{1}{f-1} \left(\frac{f-2}{f-1} \right)^{f-2} \right]^{n-1}$$

Using Stirling's approximation

$$\ln m! = m \ln(m) - m + \frac{1}{2} \ln(2\pi m)$$

$$\begin{aligned} \ln N_n = \ln N + f \ln \frac{f-2}{f-1} + \ln f + [(fn-n) \ln(fn-n) - (fn-n) + \frac{1}{2} \ln(2\pi(fn-n))] - [n \ln n - n + \frac{1}{2} \ln(2\pi n)] - \\ [(fn-2n+2) \ln(fn-2n+2) - (fn-2n+2) + \frac{1}{2} \ln(2\pi(fn-2n+2))] + (n-1) \ln \left[\frac{1}{f-1} \left(\frac{f-2}{f-1} \right)^{f-2} \right] \end{aligned}$$

Writing

$$(fn-2n+2) = n(f-2) \left[1 + \frac{2}{n(f-2)} \right]$$

the term

$$\begin{aligned} (fn-2n+2) \ln(fn-2n+2) = n(f-2) \left[1 + \frac{2}{n(f-2)} \right] [\ln n(f-2) + \ln \left[1 + \frac{2}{n(f-2)} \right]] \approx \\ n(f-2) \ln n(f-2) + 2 \ln n(f-2) - n(f-2) \left[1 + \frac{2}{n(f-2)} \right] \frac{2}{n(f-2)} \approx n(f-2) \ln n(f-2) + 2 \ln n(f-2) - 2 \end{aligned}$$

and

$$\frac{1}{2} \ln(2\pi(fn-2n+2)) = \frac{1}{2} \ln(2\pi n(f-2)) + \frac{1}{2} \ln \left[1 + \frac{2}{n(f-2)} \right] \approx \frac{1}{2} \ln(2\pi n(f-2)) - \frac{1}{n(f-2)}$$

We thus find

$$\begin{aligned} \ln N_n/N = f \ln \frac{f-2}{f-1} + \ln f + [n(f-1) \ln n + n(f-1) \ln(f-1) - (fn-n) + \frac{1}{2} \ln(2\pi(fn-n))] - [n \ln n - n + \frac{1}{2} \ln(2\pi n)] \\ - [n(f-2) \ln n + n(f-2) \ln(f-2) - n(f-2) + \frac{1}{2} \ln(2\pi(f-2)n) + 2 \ln[n(f-2)] - 2 - \frac{1}{n(f-2)}] \\ + (n-1) \ln \frac{1}{f-1} + (n-1)(f-2) \ln \left(\frac{f-2}{f-1} \right) \end{aligned}$$

and

$$\begin{aligned}
\ln(N_n/N) &= f \ln \frac{f-2}{f-1} + \ln f + [nf \ln n - \cancel{n \ln n} + n(f-1) \ln(f-1) - nf + \cancel{\kappa} + \frac{1}{2} \ln(2\pi n) + \frac{1}{2} \ln(2\pi(f-1))] \\
&\quad - [\cancel{n \ln n} - \cancel{\kappa} + \frac{1}{2} \ln(2\pi n)] - \\
&= [nf \ln n - \cancel{2 \ln n} + n(f-2) \ln(f-2) - nf + \cancel{2\kappa} + \frac{1}{2} \ln(2\pi n) + \frac{1}{2} \ln(2\pi(f-2)) + 2 \ln[n(f-2)] - 2 - \frac{1}{n(f-2)}] \\
&\quad + (n-1) \ln \frac{1}{f-1} + (n-1)(f-2) \ln \left(\frac{f-2}{f-1} \right)
\end{aligned}$$

$$\begin{aligned}
\ln(N_n/N) &= f \ln(f-2) - f \ln(f-1) + \ln f + \cancel{nf \ln n} + n(f-1) \ln(f-1) - \cancel{nf} + \frac{1}{2} \ln(2\pi) + \frac{1}{2} \ln(f-1) \\
&\quad - \cancel{nf \ln n} - n(f-2) \ln(f-2) + \cancel{nf} - \frac{1}{2} \ln(2\pi n) - \frac{1}{2} \ln(2\pi) - \frac{1}{2} \ln(f-2) - 2 \ln[n(f-2)] + 2 + \frac{1}{n(f-2)} - (n-1) \ln(f-1) + \\
&\quad (n-1)(f-2) \ln(f-2) - (n-1)(f-2) \ln(f-1)
\end{aligned}$$

Grouping the terms in $\ln(f-1)$ and in $\ln(f-2)$,

$$\begin{aligned}
\ln(N_n/N) &= \ln(f-2) [f - n(f-2) - \frac{1}{2} + (n-1)(f-2) - 2] \\
&\quad + \ln(f-1) [-f + n(f-1) + \frac{1}{2} - (n-1) - (n-1)(f-2)] \\
&\quad + \ln f - \frac{1}{2} \ln(2\pi) - \frac{1}{2} \ln n - 2 \ln n + \frac{1}{n(f-2)}
\end{aligned}$$

one finds

$$\begin{aligned}
\ln(N_n/N) &= -\frac{1}{2} \ln(f-2) \\
&\quad - \frac{1}{2} \ln(f-1) \\
&\quad + \ln f - \frac{1}{2} \ln(2\pi) - \frac{5}{2} \ln n + \frac{1}{n(f-2)}
\end{aligned}$$

hence a power-law for large n . For large n $e^{-\frac{1}{n(f-2)}} = 1$ and

$$N_n(p^c) = N \frac{f}{\sqrt{(f-1)(f-2)2\pi}} n^{-\frac{5}{2}}$$

2.1 Fractal dimension of loop-less clusters

The gyration radius of a loop-less cluster can be calculated using the Kramer theorem, evaluating the number of ways one can split the cluster in two parts composed by N_1 and $N - N_1$ monomers. The result of the calculation, available on the Rubinstein and Colby gives

$$\langle R_g^2 \rangle = \sqrt{\frac{\pi(f-1)}{8(f-2)}} b^2 N^{1/2}$$

corresponding to an unphysical fractal dimension of $D_f = 4$. The cluster of branched polymers is significantly smaller than the one of a linear polymer with the same number of monomers. The density of the branched polymers increases with N !

2.2 Another case where only the sol exists: *hyperbranched polymers*

Consider the case of N molecules with f reactive sites, of which one is of type A and $f - 1$ of type B with only possible AB links.

If we define $\#_b$ the number of bonds in the system, then we can immediately write

$$p_A = \frac{\#_b}{N} \quad p_B = \frac{\#_b}{N(f-1)}$$

where p_A and p_B are the probabilities that a site A and B has reacted. There exists then a relation between p_A and p_B given by, eliminating $\#_b$ from the two previous expressions,

$$p_A = (f-1)p_B$$

When all A sites have reacted, $p_A = 1 = p_B(f-1) = 1$, and then p_B is $1/(f-1)$. This is thus the largest value p_B can assume. The fraction of sites A that have not reacted is $1 - p_B(f-1)$.

Assuming absence of bond loops, each bond decreases by one the number of clusters and hence

$$N_{clusters}(p) = N - \#_b = N[1 - p_B(f-1)]$$

An estimate of the average cluster size dimension is then

$$\frac{N}{N_{clusters}} = \frac{1}{1 - p_B(f-1)}$$

The average size of the clusters diverges when $p_B = 1/(f-1)$, that is when all A have reacted. Beyond percolation you can't go!

Let's look at how to calculate the cluster size distribution, that is the number of clusters composed by n monomers. This term has a combinatorial contribution and an "energetic" contribution, linked to the number of bonds. A cluster of size n has only ONE unreacted A site and $n - 1$ sites B reacted, out of a total of $n(f-1)$. Calling a_n the combinatorial term, the $n - 1$ sites that reacted

make a contribution p^{n-1} and the $n(f-1) - (n-1)$ sites that have not reacted to a contribution $(1-p)^{n(f-1)-(n-1)}$

$$N_n = A a_n p^{n-1} (1-p)^{n(f-1)-(n-1)} = A a_n p^{n-1} (1-p)^{n(f-2)+1} =$$

where A , n independent, will be fixed by the normalization. Differently from the 1-d case, this time the prefactor a_n of the cluster size distribution is size dependent, since the properties of the cluster perimeter changes with the cluster size.

The degeneration a_n is the number of ways one can bind n monomers, with $n-1$ bonds. Let's assume we enumerate the particles (we make them distinct, remembering at the end to divide the result by $n!$). Then we select the $n-1$ bonds in the system. We can choose the first B in $n(f-1)$ modes, the second in $n(f-1)-1$ modes. etc. Also, we have to divide by $(n-1)!$ since we need the list of the $n-1$ bonded B , independently from their order in the list.

The total number of ways is

$$\frac{n(f-1)[n(f-1)-1]\dots[n(f-1)-(n-2)]}{(n-1)!} = \frac{[n(f-1)]!}{(n-1)![n(f-1)-(n-1)]!}$$

Next we pick the first bonded B and we link it with one of the $n-1$ monomers. Then we pick the second B in the list and we connect it to one of the $n-2$ remaining monomers. The last B will be connected to the last remaining monomer. This adds an additional $(n-1)!$ number of ways. Finally we need to divide by $n!$ to eliminate the distinguishability of the particles. Thus

$$a_n = \frac{[n(f-1)]!}{[n(f-2)+1]n!}$$

and

$$N_n = A \frac{[n(f-1)]!}{[n(f-2)+1]n!} p^{n-1} (1-p)^{n(f-2)+1} = \frac{1-p}{p} A \frac{[n(f-1)]!}{[n(f-2)+1]n!} [p^n (1-p)^{f-2}]^n$$

It is possible to show that

$$\sum_{n=1}^{\infty} N_n = A$$

which leads to the identification of A with the number of clusters in the system, $A = N_{cluster} = N[1 - p_B(f-1)]$

To simplify the calculations of the moments of N_n let's define $x \equiv p(1-p)^{f-2}$ and

$$B_n = \frac{[n(f-1)]!}{[n(f-2)+1]n!} x^n$$

such that $N_n = B_n \frac{1-p}{p} N_{cluster}$. The successive moments of the distribution B_n are defined as

$$\Sigma_k \equiv \sum_{n=1}^{\infty} n^k B_n$$

Note that, taking the derivative with respect to p

$$\begin{aligned} \frac{d}{dp} \Sigma_k &= \frac{d}{dp} \sum_{n=1}^{\infty} n^k B_n = \frac{d}{dp} \sum_{n=1}^{\infty} n^k \frac{[n(f-1)]!}{[n(f-2)+1]!n!} x^n = \sum_{n=1}^{\infty} n^k \frac{[n(f-1)]!}{[n(f-2)+1]!n!} \frac{d}{dp} x^n \\ &= \sum_{n=1}^{\infty} n^k \frac{[n(f-1)]!}{[n(f-2)+1]!n!} \left[x^n \frac{d}{dp} x^n \right] = \sum_{n=1}^{\infty} n^k \frac{[n(f-1)]!}{[n(f-2)+1]!n!} \frac{d}{dp} x^n = \\ &= \sum_{n=1}^{\infty} n^k \frac{[n(f-1)]!}{[n(f-2)+1]!n!} n x^{n-1} \frac{dx}{dp} = \Sigma_{k+1} \frac{1}{x} \frac{dx}{dp} \end{aligned}$$

which gives the following recurrent relation

$$\Sigma_k = x \frac{\partial \Sigma_{k-1}}{\partial p} \frac{\partial p}{\partial x}.$$

The derivative $\frac{\partial p}{\partial x}$ can be calculated as

$$\frac{\partial p}{\partial x} = \frac{1}{\partial x / \partial p} = \frac{1}{(1-p)^{f-2} - p(f-2)(1-p)^{f-3}} =$$

multiplying numerator and denominator by $p(1-p)$ and remembering that $x \equiv p(1-p)^{f-2}$

$$= \frac{p(1-p)}{p(1-p)^{f-1} - p^2(f-2)(1-p)^{f-2}} = \frac{p(1-p)}{x[1-p(f-1)]}$$

We know already that $\Sigma_0 = \frac{p}{1-p}$. Then, using the recurrence expression

$$\Sigma_1 = x \frac{\partial \Sigma_0}{\partial p} \frac{\partial p}{\partial x} = x \frac{1}{(1-p)^2} \frac{p(1-p)}{x[1-p(f-1)]} = \frac{p}{(1-p)[1-p(f-1)]}$$

Then, as expected

$$\sum_n n N_n = \frac{1-p}{p} N_{cluster} \Sigma_1 = \frac{1-p}{p} N_{cluster} \frac{p}{(1-p)[1-p(f-1)]} = N$$

The average cluster size \bar{N} , defined as $N/N_{cluster}$ is

$$\bar{N} = \frac{\Sigma_1}{\Sigma_0} = \frac{1}{1-p(f-1)}$$

The second moment S can be calculated analogously. Since

$$\Sigma_2 = x \frac{\partial \Sigma_1}{\partial p} \frac{\partial p}{\partial x} = x \frac{1-p^2(f-1)}{(1-p)^2[1-p(f-1)]^2} \frac{p(1-p)}{x[1-p(f-1)]} =$$

$$\frac{(1 - p^2(f - 1))p}{(1 - p)[1 - p(f - 1)]^3}$$

then

$$S = \frac{\Sigma_2}{\Sigma_1} = \frac{1 - p^2(f - 1)}{[1 - p(f - 1)]^2}$$

S diverges at the percolation transition $p = \frac{1}{f-1}$ with exponent -2 .

It is also very interesting to look at the shape of the cluster size distribution close to percolation. N_n develops a power-law behavior with exponent -1.5 and an exponential cut-off. Indeed, if we express

$$N! \approx \sqrt{2\pi N} N^N \exp(-N) \quad (\text{Stirling})$$

then

$$a_n = \frac{1}{(f-2)n+1} \frac{[(f-1)n]!}{n![(f-2)n]!} \approx \frac{1}{(f-2)n+1} \frac{\sqrt{2\pi(f-1)n} [(f-1)n]^{[(f-1)n]} \exp(-[(f-1)n])}{\sqrt{2\pi n} n^n \exp(-n) \sqrt{2\pi[(f-2)n]} [(f-2)n]^{[(f-2)n]} \exp(-[(f-2)n])}$$

$$\frac{1}{(f-2)n+1} \frac{\sqrt{(f-1)n} [(f-1)n]^{[(f-1)n]}}{\sqrt{n} n^n \sqrt{2\pi[(f-2)n]} [(f-2)n]^{[(f-2)n]}} = \frac{1}{(f-2)n+1} \sqrt{\frac{f-1}{2\pi(f-2)n}} \frac{(f-1)^{(f-1)n}}{(f-2)^{(f-2)n}}$$

Defining with ϵ the relative distance from the percolation point

$$\epsilon = \frac{p - p_c}{p_c} = (f-1)p - 1 \quad \rightarrow \quad p = \frac{1 + \epsilon}{f-1} \quad \text{and} \quad 1 - p = \frac{f-2-\epsilon}{f-1} = \frac{f-2}{f-1} \left(1 - \frac{\epsilon}{f-2}\right).$$

Converting to ϵ

$$p^{n-1} (1-p)^{(f-2)n+1} = \left(\frac{1+\epsilon}{f-1}\right)^{n-1} \left[\frac{f-2}{f-1} \left(1 - \frac{\epsilon}{f-2}\right)\right]^{(f-2)n+1}$$

$$= \frac{f-2}{1+\epsilon} \left(1 - \frac{\epsilon}{f-2}\right) \left[\left(\frac{1+\epsilon}{f-1}\right) \frac{(f-2)^{f-2}}{(f-1)^{f-2}} \left(1 - \frac{\epsilon}{f-2}\right)^{f-2}\right]^n$$

The small negative values of ϵ can be neglected outside the square bracket and we can approximate $1 + \epsilon = 1$ and $1 - \epsilon/(f-2) = 1$. Since the square bracket is taken to a large power n it dominates the ϵ -dependence. Expanding $[1 - \epsilon/(f-2)]^{f-2} \approx 1 - \epsilon$ to the lowest power in ϵ we find a simple form:

$$p^{n-1} (1-p)^{(f-2)n+1} \approx (f-2) \left[\frac{(f-2)^{f-2}}{(f-1)^{f-1}} (1+\epsilon) \left(1 - \frac{\epsilon}{f-2}\right)^{f-2}\right]^n \approx (f-2) \frac{(f-2)^{n(f-2)}}{(f-1)^{n(f-1)}} [(1+\epsilon)(1-\epsilon)]^n$$

$$= \frac{(f-2)^{n(f-2+1)}}{(f-1)^{n(f-1)}} (1 - \epsilon^2)^n \approx \frac{(f-2)^{n(f-2+1)}}{(f-1)^{n(f-1)}} e^{-\epsilon^2 n}$$

As a result

$$N_n(p) = a_n p^{n-1} (1-p)^{(f-2)n+1} \approx \sqrt{\frac{f-1}{2\pi(f-2)}} n^{-3/2} e^{-\epsilon^2 n}$$

This number fraction distribution has a form of a power law with an exponential cutoff at the characteristic degree of polymerization $N^* = \epsilon^{-2}$ and

$$N_n(p) \approx n^{-3/2} e^{-n/N^*}$$

Just as for linear condensation polymers, the simple statistics presented above assume there are no intramolecular reactions. This assumption is never really correct. For linear polymers, the assumption gets progressively better for longer chains. However, for hyperbranched polymers it gets worse for species with large degrees of polymerization, since most of the unreacted B groups near an unreacted A will be on the same polymer. Properly including intramolecular reactions is a difficult and important problem. The molar mass distribution of hyperbranched polymers does not follow the simple statistics presented here because of intramolecular reactions.

3 Ipotesi di scaling

Quanto abbiamo imparato in una dimensione ed in Bethe suggerisce una validita' generale di $n_s(p)$ vicino p_c . La teoria della percolazione postula che $n_s(p)$ sia scrivibile vicino p_c come

$$n_s(p) \sim s^{-\tau} f[s^\sigma(p - p_c)] \quad (45)$$

dove $f[z]$ e' una funzione di scala, dipendente dal modello, con delle opportune proprieta'. Vediamo come dal cluster size distribution cosi definito (esponenti τ e σ) nascono le relazioni con gli esponenti β e γ . La relazione con γ si ottiene ripetendo quanto fatto per il calcolo di S si trova

$$\gamma = (\tau - 3)/\sigma \quad (46)$$

Senza alcuna pretesa di eccessiva formalita', possiamo ricavare la relazione per P_∞ a partire dal fatto che $P_\infty + \sum s n_s = p$. Poiche a' p_c , $P_\infty = 0$ possiamo scrivere, sottraendo l' espressione valutata a $p = p_c$,

$$P_\infty + \sum s(n_s - n_s(p_c)) = p - p_c \quad (47)$$

o, nell'ipotesi di scaling, trascurando termini in $O(p - p_c)$ (che se del caso possono essere aggiunti a posteriori)

$$P_\infty = \int s^{1-\tau} (f[0] - f[z]) ds \quad (48)$$

Passando da ds a dz con $dz = \sigma s^{\sigma-1}(p - p_c)ds = z/s ds$

$$P_\infty = \int s^{2-\tau}(f[0] - f[z])dz/z = (p - p_c)^{-\frac{2-\tau}{\sigma}} \int z^{(2-\tau)/\sigma}(f[0] - f[z])dz/z \quad (49)$$

$$P_\infty \sim (p - p_c)^{-\beta} \sim (p - p_c)^{-(2-\tau)/\sigma} \quad (50)$$

da cui

$$\beta = \frac{2 - \tau}{\sigma} \quad (51)$$

4 The cluster distribution close to p_c

Near p_c the system is composed of clusters of all sizes. These clusters have a radius of giration R_s that scales with the size of the cluster s . If they were compact clusters we would already know that $R_s \sim s^{\frac{1}{d}}$. But in principle, branched objects such as percolation clusters they can scale with different exponents $D < d$. In general we assume $R_s \sim s^{\frac{1}{D}}$. The fractal dimension D of the clusters controls the critical exponent for the divergence of the connectivity length. In fact, connectivity measures the average size of clusters.

We define the connectivity length as

$$\xi^2 = \frac{\sum_s R_s^2 s^2 n_s}{\sum_s s^2 n_s} \quad (52)$$

where each size s cluster contributes with s^2 distances. We are therefore calculating the average distance (squared) of all connected pairs). Immediately we see, with the same techniques as before, that

$$\xi^2 = \frac{(p - p_c)^{-\frac{2/D+3-\tau}{\sigma}}}{(p - p_c)^{-\frac{3-\tau}{\sigma}}} \quad (53)$$

from which

$$\xi \sim (p - p_c)^{-\nu} = (p - p_c)^{-\frac{1}{D\sigma}} \quad (54)$$

giving

$$\nu = \frac{1}{D\sigma} \quad (55)$$

4.1 Summary of the exponents

Bethe: $\tau = 5/2, \sigma = 1/2, D = 4$.

3-d $\tau = 2.18, \sigma = 0.45, D = 2.53$.

Connections between geometric and percolation exponents

$$\gamma = \frac{3 - \tau}{\sigma} \tag{56}$$

$$\beta = \frac{\tau - 2}{\sigma} \tag{57}$$

$$\nu = \frac{1}{D\sigma} \tag{58}$$