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Percolation in correlated site–bond Bethe lattices

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Abstract. Percolation probabilities are obtained for site–bond Bethe lattices where the interconnection of sites and bonds is restricted by a correlation function which depends on the overlap, Ω , between site and bond probability distributions. The behaviour of the percolation phase diagram and percolation probabilities as Ω changes is discussed. The model presents interesting and qualitatively new features in comparison with a classical (non-correlated) site–bond percolation process.

1. Introduction

The mixed site–bond percolation problem has been extensively studied, both due to its theoretical importance and to its many applications in the field of technology, such as polymer gelation, capillary phenomena in porous media, fracture of porous concrete by cracks, and others [1–4]. In random site–bond percolation both sites and bonds in a lattice are randomly occupied and one requires for connected clusters that the sites are joined by occupied bonds and the bonds are joined by occupied sites [5–9]. However, the degree of randomness is usually limited in natural phenomena by correlations, which sometimes lead to a qualitatively different behaviour. Our purpose here is to study the percolation properties of a site–bond lattice in which the characteristic properties of these two entities are statistically described by a joint probability distribution involving a correlation function. To be specific, we shall base our discussion on a site–bond correlated model which has proven to be useful in the description of porous media [10–12] and is easily applicable to other problems, such as the behaviour of adsorbates on energetically heterogeneous surfaces, polymer gelation, and others [13–15]. We shall use a Bethe lattice, since this will allow an analytical approximate solution and a description of percolation probabilities valid, in a qualitative sense, for other lattices.

2. Model of correlated porous network

We represent a porous material by a network of interconnected sites (voids) and bonds (necks) of effective radii R_S and R_B , respectively, distributed according to

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frequency probability functions $F_S(R_S)$ and $F_B(R_B)$, [10]. The number of bonds emerging from a given site is the connectivity z of that site. For simplicity it is assumed that z is the same for all the sites. We suppose that site and bond sizes are statistically described by their frequency functions, $F_S(R)$ and $F_B(R)$, such that $F_S(R) dR (F_B(R) dR)$ is the probability of finding a site (bond) of size between R and $R + dR$. We can introduce the site and bond distribution functions, $S(R)$ and $B(R)$:

$$\begin{aligned} S(R) &= \int_0^R F_S(R) dR \\ B(R) &= \int_0^R F_B(R) dR \end{aligned} \quad (1)$$

representing the probability of finding a site or a bond, respectively, of a size smaller than or equal to R .

In order to build the site-bond network we adopt the following Construction Principle: for a given site, its size is always greater than, or at least equal to, the size of any of its z bonds. To ensure that all the sites corresponding to a given site distribution can be linked together, it is essential that all the bonds have sizes sufficiently small, such that

$$B(R) \geq S(R) \quad \text{for all } R. \quad (2)$$

Thus the bond size distribution curve must lie to the left of that corresponding to the sites. Overlap between the frequency curves is allowed (meaning that there exist some bonds of size R greater than that of some sites not connected to them). When sites and bonds are brought together to form a network, they cannot be chosen independently. The fact that sites and bonds are not interconnected completely at random can be taken into account by assuming that the site-bond connected pairs are statistically described by the joint distribution function:

$$F(R_S, R_B) dR_S dR_B = F_S(R_S) F_B(R_B) \phi(R_S, R_B) dR_S dR_B \quad (3)$$

where $F(R_S, R_B) dR_S dR_B$ is the probability of finding a site whose radius is in the range $(R_S, R_S + dR_S)$, connected to a bond whose radius is in the range $(R_B, R_B + dR_B)$; and $\phi(R_S, R_B)$ is a correlation function characterizing the porous medium and carrying valuable information related to the 'genesis' of the structure. If $\phi = 1$ for all the values of R_S and R_B , the events of finding R_S and R_B would be independent and the network would be built completely at random. $\phi \neq 1$ means that these events are correlated. The fact that a bond of size R_B cannot be connected to the site of size $R_S < R_B$ is then taken into account by the condition

$$\phi(R_S, R_B) = 0 \quad \text{for } R_S < R_B. \quad (4)$$

An expression for the correlation function can be developed by assuming a method of generation of what are the fundamental building blocks of the network, namely a site with its z bonds, which will build up the complete network once they are brought together.

We chose sites of increasing size, starting with the smallest sizes, and assigned to them a set of bonds, each one of a size determined by the maximum randomness allowed by the construction principle and by the availability of bonds. If condition (2) is observed, then such a procedure is always possible since, from the beginning, the smaller bonds have not yet been assigned to any site. This procedure continues up to the exhaustion of all the sites. An intermediate stage of such a branching process is schematically pictured in figure 1, where the site and bond frequency functions, $F_S(R)$ and $F_B(R)$, are represented with a certain degree of overlapping. At this stage, some bonds (area a') have already been assigned to sites of size smaller than R_S (area a), while bonds of size smaller than R_S (area b'), randomly chosen from the available ones (area c'), are going to be assigned to sites of size between R_S and $R_S + dR_S$ (area b). The function ϕ , which guarantees that no unmatched sites or bonds are left after the assignment procedure has been completed, is given by [10]

$$\phi(R_S, R_B) = \begin{cases} \frac{1}{B(R_S) - S(R_S)} \exp\left(-\int_{S(R_B)}^{S(R_S)} \frac{dS}{B-S}\right) & \text{for } R_S \geq R_B \\ 0 & \text{for } R_S < R_B. \end{cases} \quad (5)$$

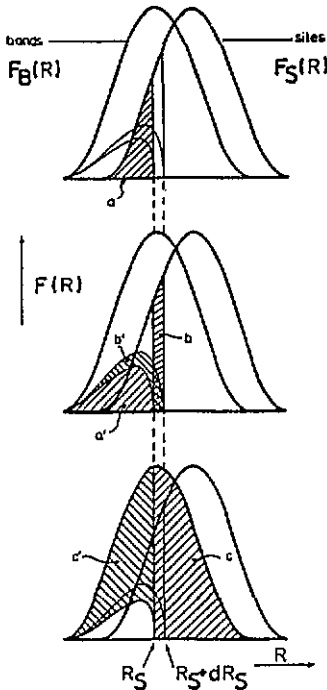


Figure 1. A geometrical interpretation of the rule by which bonds are assigned to sites.

If the inverse procedure had been followed, namely to take bonds from the larger to the smaller sizes, and then assign to them site sizes with the maximum randomness allowed by the construction principle, we would have obtained for the correlation

function:

$$\phi(R_S, R_B) = \begin{cases} \frac{1}{B(R_B) - S(R_B)} \exp\left(-\int_{B(R_B)}^{B(R_S)} \frac{dB}{B-S}\right) & \text{for } R_S \geq R_B \\ 0 & \text{for } R_S < R_B. \end{cases} \quad (6)$$

As can be easily shown, both expressions (5) and (6) for the correlation function are completely equivalent.

We remark that these expressions for ϕ are calculated in such a way that the maximum degree of randomness is obtained in the network. That is, ϕ calculated in this way produces the maximum number of possible representations in a statistical ensemble of porous networks whose site and bond frequency functions are held constant. We call this a 'verisimilar' network.

The dual distribution, equation (3), is now completely determined and it is illustrative to show, in a qualitative way, how different kinds of porous structure are generated by a few typical site-bond distributions with different degrees of overlap Ω (we realize that the overlap degree is related to the correlation function ϕ). In figure 2(a), with $\Omega = 0$, we have an uncorrelated structure where sites and bonds are very well differentiated entities randomly assigned to each other. In figure 2(c), with $\Omega \simeq 1$, we have the opposite case, namely a very correlated structure, where bonds connected to a given site are of almost the same size as that of the site. In practice, this structure can be considered as a collection of macroscopic domains of uniform pore size. In figure 2(b), with $\Omega \simeq 0.5$, we have an intermediate situation, where we find a variety of interconnected pore sizes (a given site can be connected to bonds ranging from very small to a size similar to its own) forming a quite intricate structure with a certain short-range order. This intermediate case may be representative of the great majority of porous media. It is to be expected that these different porous structures will present a different percolation behaviour, which will be shown in the next section.

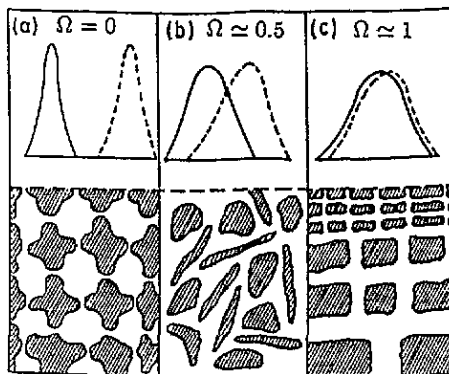


Figure 2. Three kinds of porous structure determined by different values for the overlap Ω .

In the simple case where sites and bonds are uniformly distributed:

$$F_S(R_S) = \begin{cases} 1/\Delta & \text{for } s \leq R_S \leq s + \Delta \\ 0 & \text{otherwise} \end{cases} \quad (7)$$

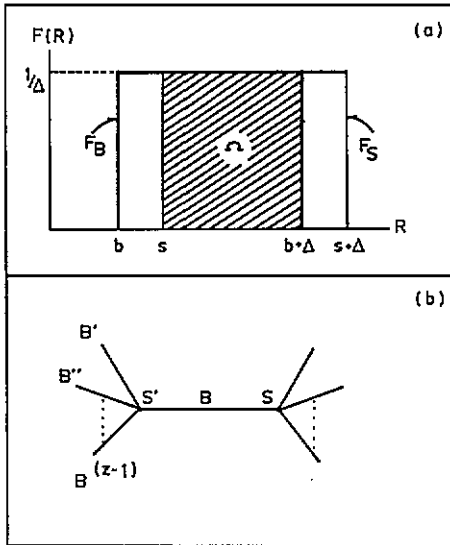


Figure 3. (a) Uniform size distributions of sites and bonds showing the overlap Ω between them. (b) The Bethe lattice of coordination number z .

$$F_B(R_B) = \begin{cases} 1/\Delta & \text{for } b \leq R_B \leq b + \Delta \\ 0 & \text{otherwise.} \end{cases} \quad (8)$$

As illustrated in figure 3(a), the correlation function takes the simple form

$$\phi(R_S, R_B) = \begin{cases} \exp[-(R_S - s)/(1 - \Omega)]/(1 - \Omega) & \text{for } R_B \leq s, R_S \leq b + \Delta \\ \exp[-\Omega/(1 - \Omega)]/(1 - \Omega) & \text{for } R_B \leq s, R_S > b + \Delta \\ \exp[-(R_S - R_B)/(1 - \Omega)]/(1 - \Omega) & \text{for } R_B > s, R_S \leq b + \Delta \\ \exp[-(b + \Delta - R_B)/(1 - \Omega)]/(1 - \Omega) & \text{for } R_B > s, R_S > b + \Delta \end{cases} \quad (9)$$

where Ω is the overlap between $F_S(R_S)$ and $F_B(R_B)$, represented by the shaded area in figure 3(a). This parameter is now the one carrying the most valuable information on the physical characteristics of the porous network and our objective is to study how it affects the percolation properties of such a correlated network.

3. Percolation properties of the Bethe lattice

In order to study the percolation properties of the site-bond network we must define when a site (or a bond) is considered to be 'occupied' (according to the percolation terminology). However, the most suitable definition will depend upon the real process to be considered. For example, in the case of mercury porosimetry [16], at a given mercury pressure, a given site (bond) can be invaded by mercury if it is connected to an already invaded bond (site) and if its radius $R_S(R_B)$ is greater than the critical Laplace radius $c_S(c_B)$ corresponding to that pressure. The critical radius may be

different for sites and for bonds since it depends on the pore geometry (for example, sites can be spherical and bonds cylindrical).

We choose the following definition which replaces the word 'occupied' by 'open': a site (bond) is considered to be open if its radius is greater than a critical radius $c_S(c_B)$. Accordingly we define the following elementary probabilities:

$$p_S = \int_{c_S}^{s+\Delta} F_S(R_S) dR_S = \text{probability of finding an open site} = \{0\}$$

$$p_{\bar{S}} = 1 - p_S = \text{probability of finding a closed site} = \{\emptyset\}$$

$$p_B = \int_{c_B}^{b+\Delta} F_B(R_B) dR_B = \text{probability of finding an open bond} = \{-\}$$

$$p_{\bar{B}} = 1 - p_B = \text{probability of finding a closed bond} = \{+\}$$

and, in a similar way, for greater clusters:

$$p_{SB} = p_{BS} = \{0-\} = \int_{c_S}^{s+\Delta} dR_S \int_{c_B}^{R_S} F_S(R_S) F_B(R_B) \phi(R_S, R_B) dR_B$$

$$p_{\bar{S}\bar{B}} = \{\emptyset-\}$$

$$p_{S\bar{B}} = \{0+\}$$

$$p_{SBS'} = \{0-0\} = \int_{c_S}^{s+\Delta} dR_S \int_{c_S}^{s+\Delta} dR_{S'} \\ \times \int_{c_B}^{\min\{R_S, R_{S'}\}} F_S(R_S) F_B(R_B) F_S(R_{S'}) \phi(R_S, R_B) \phi(R_{S'}, R_B) dR_B$$

$$p_{BSB'} = \{-0-\} = \int_{c_S}^{s+\Delta} dR_S \int_{c_B}^{R_S} dR_B \\ \times \int_{c_B}^{R_S} F_B(R_B) F_S(R_S) F_B(R_{B'}) \phi(R_S, R_B) \phi(R_S, R_{B'}) dR_{B'}$$

$$p_{S\bar{B}\bar{S}'} = \{0-\emptyset\}$$

$$p_{\bar{B}\bar{S}\bar{B}'} = \{-0+\}$$

and so on. All these probabilities are easily calculable in terms of p_S, p_B and Ω in the case of uniform distributions (equations (7) and (8)).

To obtain the percolation probabilities for a Bethe lattice of connectivity z (figure 3(b)) we follow the method introduced by Essam [17] for the random case and generalized by Coniglio [18] for correlated sites. Let $\bar{P}^S = 1 - P^S$ ($\bar{P}^B = 1 - P^B$) be the probability that every open walk from a chosen site (bond), supposedly open, be of finite length (a walk is said to be open if all its elements are open). From a given site there are z directions to follow, but there are only two from a given bond.

If $Q_S(Q_B)$ is the probability that, starting at an open site (bond), an open walk in a given direction be finite, then

$$\overline{P}^S = Q_S^z$$

$$\overline{P}^B = Q_B^2$$

where, in an approximation taking into account the correlations up to triplets, Q_S and Q_B satisfy the following equations:

$$Q_S = p_{S\overline{B}}/p_S + p_{S\overline{B}'}/p_S + (p_{SBS'}/p_S)Q_S^{z-1} \quad (10)$$

$$Q_B = p_{B\overline{S}}/p_B + (p_{BS}/p_B)[p_{BSB'}/p_{BS} + (p_{BSB''}/p_{BS})Q_B]^{z-1}. \quad (11)$$

Here we have made the further assumption that $p_{BSB'} = p_{BSB''} = \dots = p_{BSB^{(z-1)}}$ (see figure 3(b)).

In the classical case where no correlations are present, $\Omega = 0$, the well known solutions

$$\begin{cases} Q_{S,B} = 1 & \text{for } p_S p_B \leq 1/(z-1) \\ Q_{S,B} \rightarrow 0 & \text{for } p_S p_B \rightarrow 1 \end{cases}$$

are obtained.

In the general correlated case, explicit solutions can be obtained only for given values of the connectivity z . For simplicity, we take a Bethe lattice with $z = 3$. The accuracy of equations (10) and (11) varies for the different regions of the (p_S, p_B) space, since they depend on different powers of p_S and p_B . For $z = 3$ it is convenient to consider the following procedure.

(i) For $p_S \leq p_B + \alpha(1 - \Omega)$:

$$\begin{cases} Q_S = p_{S\overline{B}}/p_S + p_{S\overline{B}'}/p_S + (p_{SBS'}/p_S)Q_S^2 \\ Q_B = p_{B\overline{S}}/p_B + (p_{BS}/p_B)Q_S^2 \end{cases} \quad (12)$$

$$\quad \quad \quad (13)$$

which are solved by finding Q_S as

$$Q_S = \begin{cases} p_S/p_{SBS'} - 1 & \text{if } p_S \leq 2p_{SBS'} \\ 1 & \text{otherwise.} \end{cases}$$

(ii) For $p_S > p_B + \alpha(1 - \Omega)$:

$$\begin{cases} Q_B = p_{B\overline{S}}/p_B + (p_{BS}/p_B)[p_{BSB'}/p_{BS} + (p_{BSB''}/p_{BS})Q_B]^2 \\ Q_S = p_{S\overline{B}}/p_S + (p_{SB}/p_S)Q_B \end{cases} \quad (14)$$

$$\quad \quad \quad (15)$$

which are solved by finding Q_B as

$$Q_B = \begin{cases} (p_{BSB'}^2 - 2p_{BS}p_{BSB'} + p_B p_{BS})/p_{BSB'}^2 & \text{if } p_B \leq 2p_{BSB'} \\ 1 & \text{otherwise.} \end{cases}$$

In the above procedure, α is an arbitrary parameter whose value for an overall satisfactory solution is found to be $\alpha = 0.6$ for all values of Ω .

This allows the calculation of site and bond percolation probabilities, P^S and P^B , respectively, and the percolation threshold as a function of p_S , p_B and Ω . Typical results for the simple case of uniform site and bond distributions are shown in figures 4 and 5. The approximations made in obtaining this solution introduce errors which are typical of a mean-field type of approximation, but are difficult to estimate quantitatively. However, we are here mainly interested in the qualitative behaviour of the percolation probabilities in correlated porous structures.

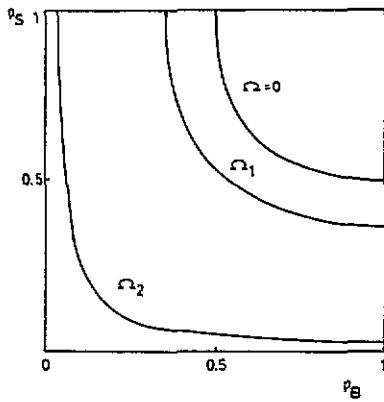


Figure 4. A percolative phase transition diagram for the correlated Bethe lattice of coordination 3, showing the transition lines for some values of the overlap where $1 > \Omega_2 > \Omega_1 > 0$.

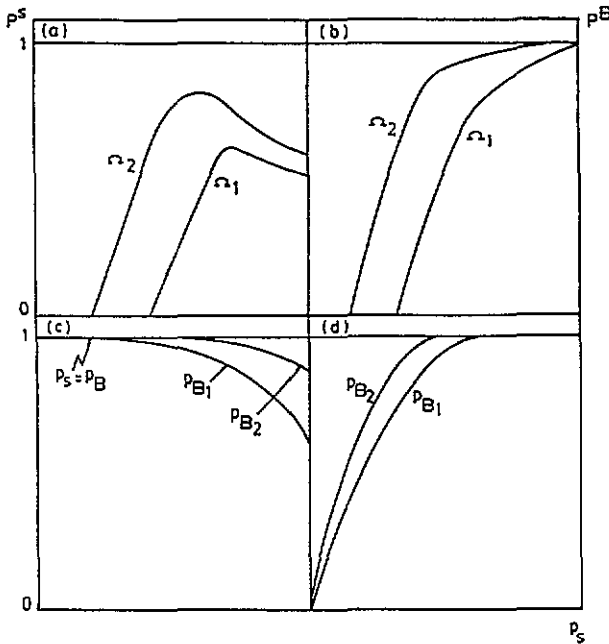


Figure 5. The behaviour of the percolation probabilities P^S and P^B , as functions of p_S : (a) and (b) for a fixed value of p_B and $1 > \Omega_2 > \Omega_1 > 0$; (c) and (d) for the extreme case $\Omega = 1$ and $p_{B2} > p_{B1}$.

4. Discussion

The phase diagram for the percolation transition, i.e. the threshold values of p_S and p_B for which the percolation probabilities P^S and P^B become > 0 , represented in figure 4, shows that the percolation region in the space (p_S, p_B) expands from the classical region for uncorrelated lattices, corresponding to $\Omega = 0$, to the whole region

($0 < p_S \leq 1$, $0 < p_B \leq 1$) for $\Omega = 1$. In fact, in the limit case $\Omega = 1$ the percolation problem has the simple solution:

(i) for

$$p_S \leq p_B \begin{cases} Q_S = 0 \\ Q_B = 1 - p_S/p_B \end{cases} \quad (\text{every open site belongs to the infinite cluster})$$

(ii) for

$$p_S > p_B \begin{cases} Q_B = 0 \\ Q_S = 1 - p_B/p_S \end{cases} \quad (\text{every open bond belongs to the infinite cluster})$$

This behaviour can be rationalized by considering that for $\Omega = 1$ correlations are so strong that the lattice splits into macroscopic (infinite) sublattices in which all connected sites and bonds have the same radii. So, if $c_B \leq c_S$ ($p_S \leq p_B$) and one starts at an open site, this is connected to z open bonds, each one of which is in turn also connected to a new open site, and so on. A symmetric argument is also valid for $c_S < c_B$ ($p_S > p_B$). Phase diagrams for $0 < \Omega < 1$ are obviously intermediate between the two extreme cases.

The behaviour of the percolation probabilities P^S and P^B , for a fixed value of p_B and as a function of p_S (figure 5) presents some most interesting features. In a classical (uncorrelated) percolation process, after the infinite cluster has been formed, the probability of a new open element (site or bond) being connected to the infinite cluster is greater than the probability of not being connected and this results in a monotonically increasing percolation probability (which measures the mass of the infinite cluster relative to the total mass of open elements).

In our site-bond correlated model, on the contrary, for a given overlap Ω , when p_S becomes greater than $p_B + (1 - \Omega)$ (c_S becomes smaller than c_B), any new open site cannot belong to the infinite cluster because the necessary open bonds to do it have already been spent and this means that the relative mass of the infinite cluster decreases with increasing p_S , producing a maximum in P^S at $p_S = p_B + (1 - \Omega)$ (figure 5(a)). The maximum does not appear in P^B (remember that here we are at a fixed value of p_B) since for $c_S < c_B$ a new open bond will always have a connected open site (figure 5(b)). Figures 5(c) and (d) represent the behaviour for the limit case $\Omega = 1$, which can be rationalized through similar arguments. A completely symmetric situation is expected for P^B and P^S , at fixed p_S , as a function of p_B .

The shifting of the percolation threshold to lower values as Ω increases and the variation of the shape of the percolation probabilities P^S and P^B as Ω changes are fundamental tools in the understanding of the behaviour of fluids in real porous materials. The ideas underlying the model presented here and some of our preliminary results have been used recently [12] in a qualitative way to explain the properties of the hysteresis loops observed in mercury porosimetry and nitrogen sorption for a great variety of porous materials.

Acknowledgment

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