

VII. Porous Media

Lecture 32: Percolation

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References: S. Torquato, *Random Heterogeneous Materials* (Springer 2002)
D. Stauffer, *Introduction to Percolation Theory*

In electrochemical energy systems, porous electrodes are generally used to maximize interfacial area to facilitate Faradaic reactions between the electron-conducting electrode matrix and the ion-conducting electrolyte. In batteries, energy density is also of concern, and can be augmented by increasing the volume fraction of active material. However, greater volume fraction means less porosity, and so lower conductivity and reduced power density. Understanding this balance requires a model of conductivity in composite materials. Here, “percolation” will refer to a connected conductive pathway in a system of multiple phases.

1. Random Microstructures

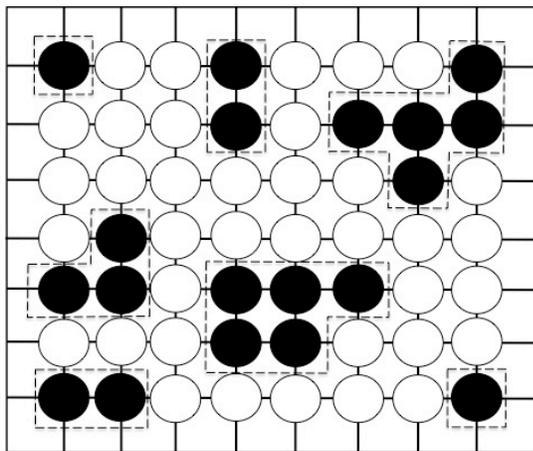


Figure 1 - Random realization of site percolation on 2D square lattice

1.1 Lattice percolation

The lattice model is the simplest description of connectivity in a random material with a given volume fraction, Φ . For discrete microstructures, $p = \Phi$ when size $\rightarrow \infty$. Clusters of connected occupied sites can be identified, and one can study statistics of the largest cluster and sites connected to boundaries as ‘ p ’ is varied. “Percolation” implies that a cluster spans to opposite boundaries, which is a prerequisite for nonzero conductivity.

The first example of a percolation model was proposed by the polymer chemist, P. Flory, in 1941 to describe the sol-gel transition, in which the removal of solvent increases the monomer concentration and promotes the formation of large polymer clusters, purely by geometrical effects of random connectivity. We have all observed this process during the heating of an egg, as the clear liquid turns white. The basic concept, however, has much broader applications.

Broadbent and Hammersley (1958) coined the term “percolation” for the phenomenon of forming a spanning cluster connecting two boundaries and developed a general mathematical theory, motivated by applications to flow in porous media. This is closer to our application of conduction in composite media and porous electrodes.

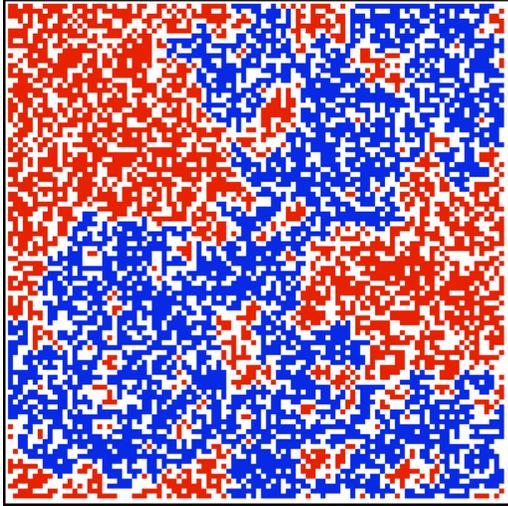


Fig. 2. Largest cluster in critical 2D site percolation – Berkeley.edu

Courtesy of Rick Durrett. Used with permission.

It is instructive to perform numerical experiments, as in the interactive online demo: <http://projects.si.umich.edu/netlearn/NetLogo4/LatticePercolation.html> This site allows you to visualize all clusters in gray and the largest cluster in red for a given realization with specific p in 2D site percolation. By sweeping p across the range 0 to 1 you can also clearly see the onset of percolation, where the largest cluster spans the system.

1.2 Continuum percolation

Lattice percolation is relevant in some systems, but most engineering materials involve amorphous structures, which require various continuum generalizations of the percolation model. The site occupation probability is then replaced by the volume fraction in microstructures generated by various stochastic algorithms. Examples include overlapping spheres, or their “swiss cheese” inverse, as shown in the figure. Packings of hard or soft spheres or other shapes may also be considered.

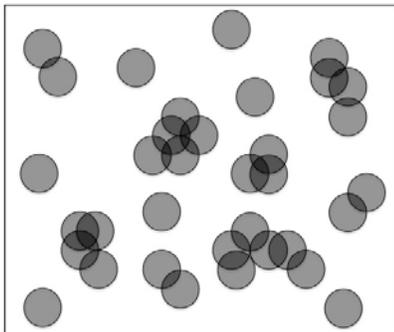


Figure 3a - Continuum percolation with overlapping spheres randomly placed in the continuum.

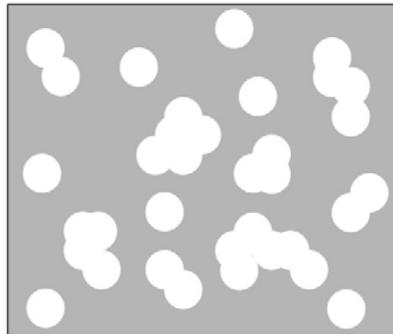


Figure 3b – The inverse “swiss cheese model” with spheres randomly cut out of the continuum.

Local heterogeneity can have a major effect on continuum percolation. For example, anisotropic overlapping shapes, such as rods, can more easily connect to each other and percolate at lower volume fractions. Polydisperse spheres have a higher threshold volume fraction for percolation, since they fill can space more easily without forming percolating clusters.

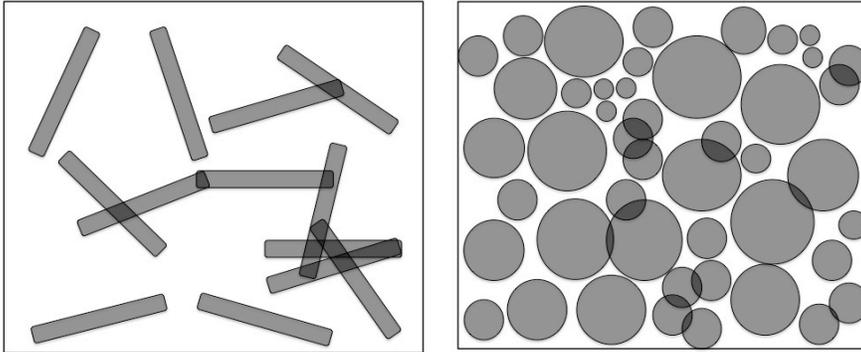


Figure 2 – Effects of local heterogeneity on percolation in random microstructures. (a) A percolating cluster of rods, which more easily forms at low volume fraction, thereby lowering the critical volume fractions percolation transition. (b) A non-percolating system of polydisperse spheres, which more easily forms at high volume fraction.

2 Percolation Transition

A remarkable property of all percolation models is that there exists a nonzero value p_c (lattice) or Φ_c (continuum) where the probability of percolation (fully spanning) jumps from 0 to 1 in an infinite system.

Let $R_N(p)$ = probability of spanning a system of size N .

N = number of sites or total volume/mean particle volume

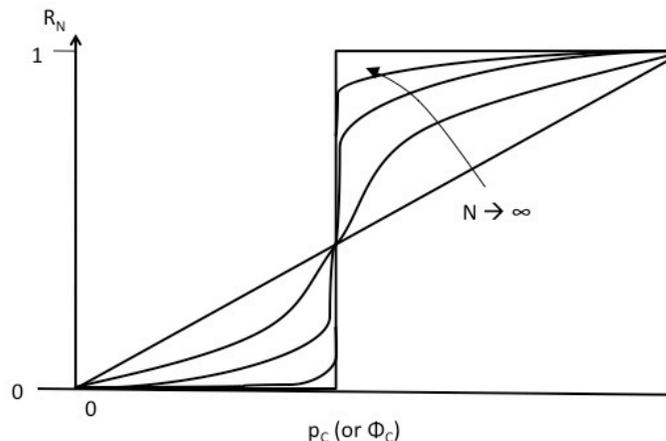
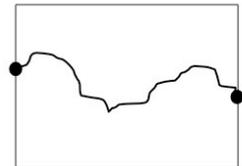
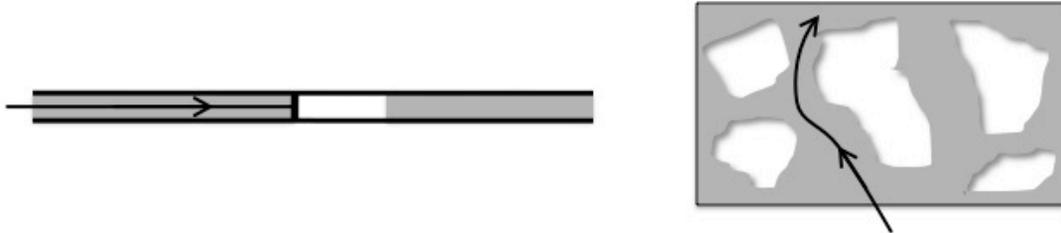


Figure 4 - Spanning probability and critical 'p'



The value of p_c depends sensitively on the model and roughly decreases with increasing dimensionality or number of neighbors (lattice). Note that $p_c = 1$ in one dimension, as any unoccupied region fully blocks conduction/percolation. As dimension and/or number of neighbors is increased, it becomes easier to get around such “road blocks.”



[Ref: Torquato]

Lattice	Dimension, d	Coordination number 'z'	p_c (site lattice) or Φ_c (continuum)
	1	2	1
Honeycomb	2	3	0.6970
Square	2	4	0.592746
Triangular	2	6	$1 - 2*\sin(\pi/8) \approx 0.657$
Overlapping disks	2	-	0.67637
Simple cubic	3	6	0.3116
Body-centered cubic	3	8	0.2464
Face-centered cubic	3	12	0.198
Overlapping spheres	3	-	0.2895
Bethe lattice (Cayly tree)	∞	z	$1/(z-1)$

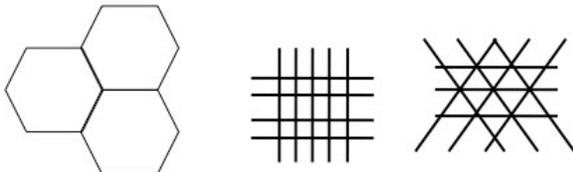


Figure 5 - 2D lattices with $z = 3, 4, 6$ from left to right.

3 Renormalization Group Estimates

A cell is “occupied” if it is spanned internally, ‘p’ is renormalized to larger length scales and can be done so recursively.

$$P_n^m = R_n * R_n * \dots * R_n(p) \approx R_n^m(p)$$

(Iterated m times). The iteration approximates the spanning probability with increasing size $N = n^m$ as in the figure $R_N(p)$ above and leads to three fixed points, $P_N \rightarrow 0, 1,$ or $p_c^{(n)}$ which satisfies

$$p_c^{(n)} = R_N(p_c^{(n)})$$

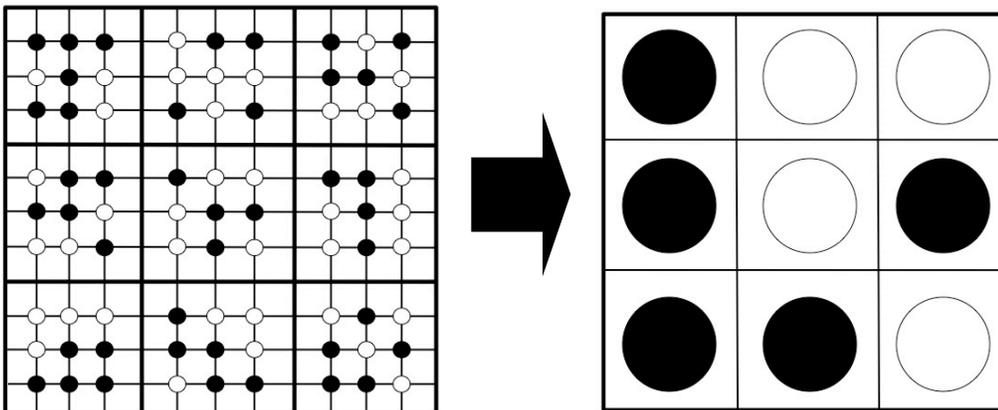


Figure 6 - $N = n^2$ sites, n cells with n sites each.

$$p_{n^2} = R_n(p_n) = R_n(R_n(p))$$

3.1 Example: Square lattice site percolation

Probability of spanning in one direction:

$$R_4(p) = p^4 + 4p^3q + 2p^2q^2$$

where $q = 1 - p$. The equation $R_4(p)$ has three solutions 0, 1, and

$$p_c^{(4)} = \frac{\sqrt{5}-1}{2} \cong 0.618 \text{ (and negative solution)}$$

which is close to the best simulation estimate, 0.592746.

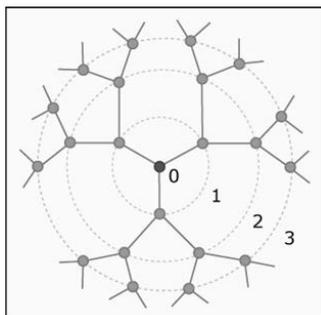


Figure 8 - $Z=3$ Bethe lattice

3.2 Example: Bethe lattice / Cayly Tree

The lattice becomes a loopless network of sites as dimensions increase with coordination number 'z.' In this case, the Renormalization Group (RG) estimate is *exact*.

$$R_z(p) = (z-1)*p^2$$

Apply this process recursively inward, starting from the outermost "branches."

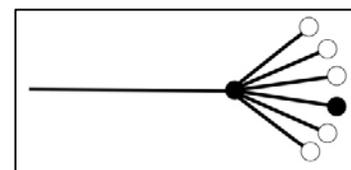


Figure 7 - White circles represent $z - 1$ neighbors

$$p = R_z(p) \rightarrow p_c = \frac{1}{z-1}$$

This shows nicely how p_c decreases with ‘z.’ Since the Bethe lattice has surface:volume ratio $\rightarrow 1$ as $N \rightarrow \infty$, this is a **lower bound** for p_c for any lattice with coordination number ‘z,’ as shown in the table.

4 Accessible Capacity

If the active phase of a battery electrode has volume fraction Φ , what fraction of the active material is connected to the current collector, and thus accessible to electrons? Assuming a percolation model, a related quantity is the “strength” of the largest cluster:

$$P_N = \frac{\text{expected size of largest cluster}}{\# \text{ of sites}} = \frac{S_N}{N}$$

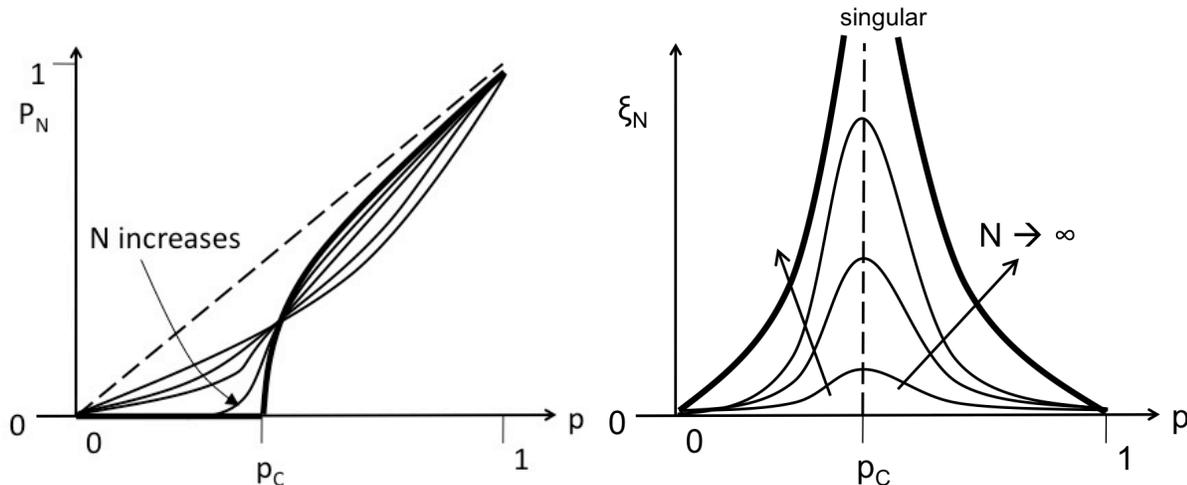


Figure 9 – (a) Strength (fraction of occupied sites) of the largest cluster and (b) correlation length, for the size of the second largest cluster, as a function of increasing system size N . In the thermodynamic limit of infinite system size, a critical point emerges where the largest-cluster strength develops a cusp, and the correlation length diverges, as in other second-order/continuous phase transitions.

Note: due to incomplete connectivity of the occupied sites, $P_N < p$ although $P_N \sim p$ as $p \rightarrow 1$.

P_N acts like an “order parameter” in continuous “phase transition” since $P_N \rightarrow 0$, $p < p_c$, $N \rightarrow \infty$.

Near p_c : $P_\infty(p) \sim (p - p_c)^\beta$ where β is a “critical exponent” believed to be “universal” for any model in the same embedding dimension.

Correlation length $\xi(p)$: Prob(x and x' are connected but not in the largest cluster) $\sim e^{-\frac{|x-x'|}{\xi}}$
 where $\xi(p)$ is the typical size of non-spanning clusters. In an infinite system, $\xi_\infty(p) \sim |p - p_c|^{-\nu}$.

When $\xi > L$ (system size, spanning clusters are *fractals* which are self-similar and have size $s \sim L^{d_f}$ where $d_f < d$ is the fractal dimension.

The largest cluster in a finite system has the scalings ($N = L^d$):

$$S_N \sim \begin{cases} \xi^{d_f} \log \frac{N}{\xi^d} & \text{Subcritical: } \xi(p) < L, p < p_c; \\ N^{\frac{d_f}{d}} & \text{Critical: } \xi(p) > L \text{ (fractal)} \\ P_\infty(p)N & \text{Supercritical: } \xi(p) < L, p > p_c \end{cases}$$

[For more precise scalings for 2D percolation and general theory, M. Z. Bazant, Phys. Rev. E 62 (2000) 1660.] In subcritical percolation, the largest cluster has a typical size ξ^{d_f} which increases logarithmically with the number of independent “correlation volumes” N/ξ^d

These results help to estimate accessible capacity for all ‘p’ (or Φ).

Note: from the critical \rightarrow supercritical transition at $\xi \sim L$ we have

$$N^{\frac{d_f}{d}} = L^{d_f} \sim \xi^{d_f} \sim (p - p_c)^{-d_f \nu} \sim P_\infty(p) \sim (p - p_c)^{\beta - d_f \nu} \rightarrow \mathbf{d - d_f = \beta/\nu}$$

“Hyperscaling relation”

So we see that d_f is not an independent critical exponent. Note: this holds for all $d \leq 6$ and the exponents match those of the Bethe lattice at $d = 6$, therefore $d_c = 6$ is the **upper critical dimension** for percolation, above which critical exponents are constant, same as a loopless structure (Bethe lattice).

5 Effective Conductivity

Suppose each occupied region has conductivity σ (for electricity, heat transfer, steady diffusion, etc.). What is the macroscopic mean conductivity, $\bar{\sigma}$? Clearly, if $L \gg \xi$, then $\bar{\sigma} = 0$ for $p < p_c$ since there are negligible spanning clusters for conduction.

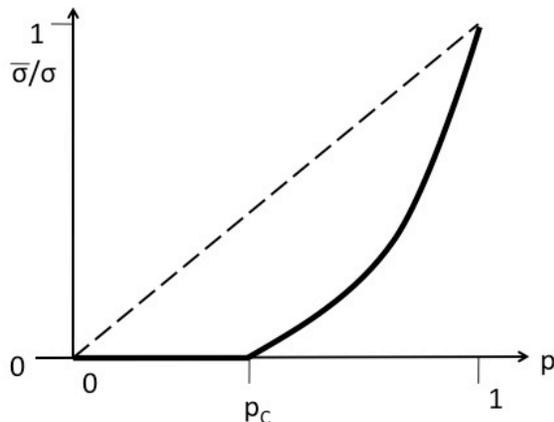


Figure 10 - Macroscopic mean conductivity

Note: $\bar{\sigma} < \sigma$ since some regions are not connected to the boundary.

Near p_c ($\xi(p) \gg L$), $\frac{\bar{\sigma}}{\sigma} \sim (p - p_c)^t$

Note: ‘t’ is much smaller than d_f , since most sites in fractal critical clusters are “dead ends” that do not contribute much conductivity. On the other hand, with loops, t is larger than d_b , the fractal dimension of the “backbone” of a spanning cluster, with all loops and dead ends removed.

Summary of percolation critical exponents:

	$d = 2$	$d = 3$	$d \geq d_c = 6$
β	$5/36$	0.41	1
ν	$4/3$	0.88	$1/2$
t	1.3	2	3
d_f	$91/48$	2.52	4
d_b	1.64	1.8	2

(Believed to be universal, depending only on the dimension of the system, d)

Given these scalings, a reasonable approximation for 3D percolation conductivity would be

$$\frac{\bar{\sigma}}{\sigma} \approx \begin{cases} \left(\frac{\Phi - \Phi_c}{1 - \Phi_c}\right)^2, & \Phi \geq \Phi_c \\ 0, & \Phi < \Phi_c \end{cases}$$

(where $\Phi_c = p_c$) since $\bar{\sigma} = \sigma$ at $\Phi = 1$, and depending on the model $\Phi_c \approx 0.2 - 0.3$ for lattices or continuum percolation with monodisperse isotropic particles or lattice cells.