Monte Carlo Simulation of Percolation in Porous Media: Global and Local Levels of Flooding

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Permeation of fluids (electrolytes and gases) in porous materials is important in batteries, fuel cells and several other electrochemical systems. In this paper, we present an elegant Monte Carlo algorithm for simulating such percolation phenomena and it is used to compute global and local levels of flooding as a function of depth. Depth profiling can be a valuable tool in studying the wettability and the flooding characteristics of porous electrodes in batteries and fuel cells and for probing the permeability of corrosive agents (such as chloride-bearing water) in concretes. It will also help in their optimal design for specific applications, since the percolation model parameter p is directly relatable to the experimental variables such as the pore-size distribution, the solid/gas and solid/liquid interfacial tensions and the pressure difference across the porous matrix.

Key words: Percolation, porous media, monte carlo simulation, depth profiling

Introduction

Percolation of fluids [1,2] represent several naturally occurring and lab-mode phenomena in micro-, meso- and nano-porous materials. A knowledge of percolation and the factors influencing it is becoming increasingly important in the development and design of material systems for optimal performance in different applications. The process of percolation is influenced by material properties such as the wettability (hydrophilicity versus hydrophobicity) as expressed through the relevant contact angle and interfacial tensions, the matrix property namely the pore size distribution and the experimentally controlled variables like the applied pressure differential across the porous matrix. In the case of porous electrodes used in batteries and fuel cells, the applied electrical potential is an additional variable to reckon with. For design and performance optimisation, the degree of percolation and its depth dependence need to be computed for different settings of these factors. For example, while the permeation of chloride-bearing water up to the steel reinforcements in concretes is detrimental to the structure [3], a better permeation of the electrolyte in batteries and fuel cells is desirable for more current and power outputs from the power source. Seepage of water, oil and gas through the Earth is another major area where percolation plays a role [4,5].

In this paper, we develop a design tool based on a Monte Carlo (MC) simulation of percolation in porous media which in turn depends on a novel algorithm for computing the global and local levels of flooding.

The model

The porous medium is modelled as a random network of capillaries. The radius of the capillaries is taken to be random having the distribution f(r). This pore size distribution function is experimentally measurable by the mercury porosimeter. Before treating the whole network, it is worthwhile to have a model for a single capillary of radius r shown in Fig.1. This figure shows capillary equilibrium existing between a gas of pressure P_g and an electrolyte of pressure P_l. For a wetting (non-wetting) liquid Cosq is positive (negative) and equilibrium requires $P_g > P_l$ ($P_g < P_l$). For a fixed pressure differential DP (DP $= P_g - P_l$), g_{lg} and q, the radius of the capillary which can maintain equilibrium is given by

$$r_e = \frac{2\,\gamma_{lg}\,Cos\theta}{\Delta P} \tag{1}$$

Clearly, if r>r_e, the wetting liquid will be expelled out of the capillary and, if r < r_e, it will "flood" the capillary. The exact reverse is true for a non-wetting liquid.
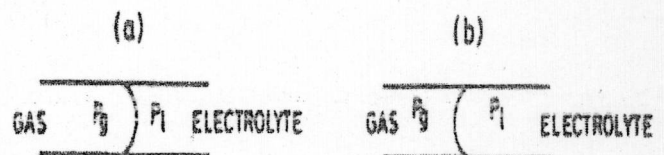

Fig.1: Capillary equilibrium in a single pore for (a) wetting and (b) non-wetting liquid

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Now we are all set to define our model parameter, which shall be hitherto referred to as the percolation parameter p, as follows.

$$p = \int_{o}^{r_e} f(r)\, dr$$

(Wetting liquid) (2)

$$p = \int_{r_e}^{\infty} f(r)\, dr$$

(Non-wetting liquid) (3)

The percolation parameter p gives the probability that a capillary randomly chosen from the pore network is open for the electrolyte to percolate into it. It is to be noted that the percolation parameter p elegantly captures all the factors influencing the percolation process as listed in the introduction. p is a probability and hence it takes values from zero to unity.

A Monte Carlo algorithm for simulating percolation on the pore network

From the model of a single pore we are now ready to construct an MC algorithm for simulating the percolation process in the entire pore network. This is a highly complex connectivity problem in that percolation in a local pore depends on its global connections. For a pore to be flooded, it should be open in the sense of equations (1) to (3) and, in addition, it must be connected to the liquid reservoir by at least one continuous chain of open pores. Unlike the closely related problem of Brownian random walk and diffusion (which has the Fokker-Planck equation) no differential law has yet been found for percolation. Hence progress in this field has been heavily dependent on Monte Carlo simulation using high-speed computers. Several algorithms have been proposed. The Hoshen-Kopelman algorithm (HKA)[6] is by for the most efficient procedure hitherto available. However, all these algorithms are academic in nature aimed at identifying percolation clusters, and computing their sizes & size distributions. None of them is capable of computing the degree of percolation as a function of depth [7] in the porous medium. This depth profiling is vital for application areas [See Introduction] where the depth dependence plays a central role. In this section, we summarise a new algorithm which we have developed for this purpose.

Table 1 shows a 10 x 10 lattice representing a porous matrix of 100 pores with its top face contacting a liquid reservoir. Each site in the lattice denotes a pore that may be open or closed in the sense of equations (1) to (3). Using random number generation, and for a fixed value of the percolation parameter p, open pores may be randomly picked and marked with a '1' and the remaining are closed pores marked with a '0'. In Table 1, p = 0.58 and the top row, with all sites marked with a '1', corresponds to the liquid reservoir.

Table 1: A 10 x 10 lattice with an additional top row, (s,e,l)'s and (c,l)'s for each row and the corresponding label of labels.

10 x 10 lattice	(s, e, l)'s	(c, l)'s
1 1 1 1 1 1 1 1 1 1	(1, 10, 1)	(10, 1)
1 1 1 1 1 1 0 1 0 0	(1, 6, 1), (8, 8, 1)	(7, 1)
1 1 1 0 0 1 1 0 0 0	(1, 3, 1), (6, 7, 1)	(5, 1)
0 0 1 1 0 0 0 0 1 0	(3, 4, 1), (9, 9, 2)	(2, 1), (1, 2)
0 0 0 0 1 1 1 0 1 1	(5, 7, 1), (9, 10, 2)	(3, 1), (2, 2)
0 1 0 1 1 1 0 1 0 0	(2, 2, 3), (4, 6, 1), (8, 8, 1)	(1, 3), (4, 1)
0 1 0 1 1 1 1 0 0 1	(2, 2, 3), (4, 7, 1), (10, 10, 4)	(1, 3), (4, 1), (1, 4)
1 0 1 1 1 1 1 1 1 0	(1, 1, 5), (3, 9, 1)	(1, 5), (7, 1)
1 1 1 1 0 1 1 1 1 1	(1, 5, 1), (7, 10, 1)	(9, 1)
1 1 0 0 0 0 1 0 1 1	(1, 2, 1), (7, 7, 1), (9, 10, 1)	(5, 1)
1 1 0 1 1 0 0 0 0 1	(1, 2, 1), (4, 5, 6), (10, 10, 1)	(3, 1), (2, 6)

Label of labels : n[1] = 1, n[2] = 2, n[3] = 1, n[4] = 4, n[5] = 1 and n[6] = 6

Now the MC simulation runs as follows. Starting with the top row, travel along each row of the lattice and identify the 1-dimensional clusters of 1's (i.e. the open pores). Stop at each such 1-D cluster and construct the triple (s,e,l) where s,e and l denote respectively the starting position, the ending position and the label of the current 1-D cluster. Assigning the label requires particular care and we follow the labelling methodology of Hoshen and Kopelman [6]. If the current 1-D cluster is not connected to any 1-D cluster in the previous row, a new label is assigned to the current cluster and this label is set to point to itself, i.e., n(label) = label; when this condition is satisfied, we say the label is good and otherwise it is a bad label. n[.] will be referred to as the label of labels array. If, on the other hand, the current 1-D cluster is connected to one or more 1-D clusters in the previous row, find their good labels (using the label of labels array) and assign the smallest one as the label of the current cluster. The connectivity check is done thus: If (s2, e2, l2) denotes a cluster in the current row and (s1, e1, l1) denotes a cluster in the previous row, then the two clusters are not connected if [e1<(s2-1) OR e2<s1] and connected otherwise.

The (s,e,l)'s thus generated are stored in an array. Two such arrays are used, one for the current row and one for the previous row.

Next, after creating all the (s,e,l)'s on a given row, scan them and club the sizes of all (s,e,l)'s having the same label into a variable c and define the corresponding double (c,l). There will be as many (c,l)'s as there are distinct labels in that row. It is these (c,l) objects which are used in the final analysis and not the (s,e,l)'s which are temporarily created and destroyed.

The final analysis proceeds as follows. We first find the good label for each and every label, using the n[.] array. The good label for each and every original label is then stored in a new array, termed "Good-labels" array.

We are now ready to carry out the Depth Profiling. Take each row and find the good label (from the good labels array) of each (c,l)'s label. If it is unity, then the 1-D clusters represented by the (c,l) object are connected to the top row (i.e. fluid reservoir) and the sizes of such (c,l)'s add up to yield the local level of flooding (LLF). LLF gives the number of pores in a particular row connected to the top row and hence "flooded". The sum of the LLF's over the rows yields the Global Level of Flooding (GLF).

Results and conclusions

Graphs of the LLF versus the row number (i.e. depth) are shown in Fig.2 for 3000 x 3000 lattice and for several values of the percolation parameter p. For small values of p, the LLF falls off monotonically with depth. Past a critical value of p, the LLF vs depth plot flattens off soon after the initial fall. This criticality is made clearly visible if we plot the GLF against p. Several GLF vs p plots were computed for different lattice sizes and a typical plot is presented in Fig.3. Clearly, the GLF remains almost zero for small values of p and suddenly shoots up at the percolation threshold.
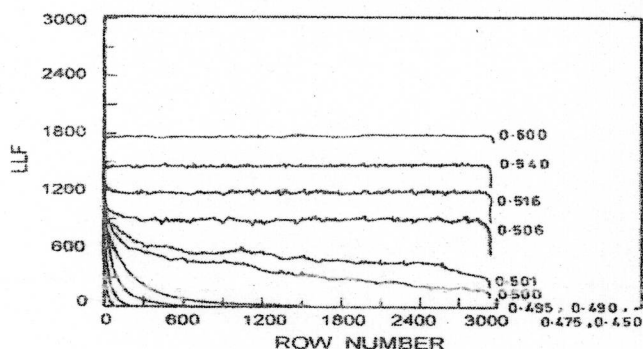

Fig.2: Local Level of Flooding(LLF) vs Row number for a 3000 x 3000 lattice for several values of P.
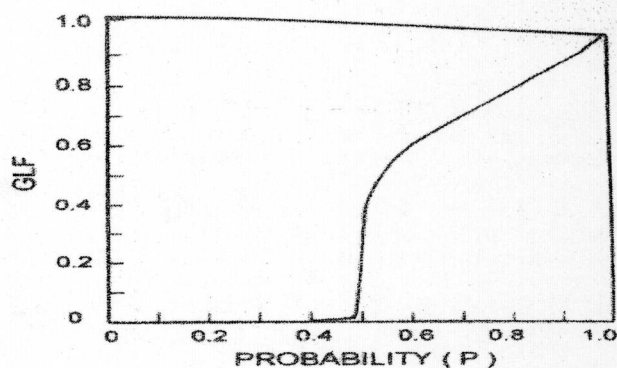

Fig .3: Global Level of Flooding (GLF) vs P for a 3000x3000 lattice

We have also carried out extensive analyses and testing [8] of the MC algorithm developed here and further compared it with the Hoshen-Kopelman algorithm. The HKA can do only cluster analysis while ours does depth profiling in addition to cluster analysis. For cluster analysis, the two algorithms match [8] in their speed and memory management capabilities. However, depth profiling is the important BONUS!

The Monte Carlo algorithm developed here is a valuable tool for depth profiling and can be used in studying the wettability and flooding characteristics of porous systems. As remarked already, the percolation model parameter p is directly related to the experimental variables, (see equations 1,2 and 3) such as the pore-size distribution, contact angle and inter facial tensions. Each setting of these variables determines a p value between zero and unity. Using this value of p, figures such as 3 and 4 can be used to predict whether or not the system is in the percolative region $(p>p_{critical})$, the extent of percolation and its depth dependence. As pointed out in the Introduction, this knowledge will help in the optimal design of porous systems for specific applications.

Symbols used

P_g	pressure on the gas side
P_l	pressure on the liquid side
q	contact angle
g_{lg}	gas-liquid interfacial tension
r	pore radius
r_c	equilibrium pore radius
f(r)	pore size distribution
p	percolation model parameter
$p_{critical}$	percolation threshold

Acknowledgement

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