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In-silico simulation of porous media: Conception and development of a greedy algorithm

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ABSTRACT

Cubic porous networks consisting of several millions of voids of different sizes are efficiently simulated through a greedy algorithm. The porous network is built on the basis of the Dual Site-Bond Model in which a cavity (site) is always larger than any of its delimiting throats (bonds). When the initial configuration of the cubic network is established by means of a random (Monte Carlo) seeding on a lattice of sites and bonds, the proper allocation of more pore elements becomes troublesome and time-consuming, and there even exists the chance of not achieving a valid pore network. The complexity of this pioneering Monte Carlo algorithm, in the best case, increases according to the third power of the number of pore elements and, in the worst case is asymptotic to infinity. Here, we have succeeded in the development of an smart non-mistake initial seeding situation of sites and bonds that behaves in the way of a greedy algorithm. An initial ordering of sites according to their sizes allows a proper assemblage of these hollows throughout the cubic lattice. From this configuration, the pore network evolves toward the most probable one by a series of legitimate random swappings between sites and bonds. The complexity of the greedy algorithm remained proportional to the cubic power of the total number of sites. In general the execution time of the greedy algorithm results to be faster than that employed with the previous Monte Carlo algorithm.

1. Introduction: the conception of a porous network from the concepts of sites and bonds

Porous media are complex systems in which a huge amount of pore entities (usually millions, billions and even trillions of them per unit mass of solid) are dispersed within the interior of a solid matrix. The term *complex* applies due to the complicated morphology that the voids can display and the intricate topological way in which they can be distributed and interconnected. The dimensions of the voids in a mesoporous solid range within the nanometric scale, i.e. from 1 nm to 50 nm. These pores are generally interconnected to each other to conform sinuous 3-D (and only occasionally simple) pathways; nevertheless, with the progress of synthetic chemical routes for the nanoscale preparation of mesoporous materials ordered 2- or 1-D porous networks have also been synthesized [1].

The importance of porous solids rests on the extensive surface area and large pore volume that these substrates can reach. Depending on the pore size and density of the solid phase, surface areas can be as high as 2600 $m^2\ g^{-1}$ and porosities as large as 99%. Obviously, in the case of catalytic or sorption applications, the values of these two parameters are strategic for reaching good performances in these processes. An ancient classification [2] of porous media involves two specimen classes: corpuscular and spongy. The corpuscular term applies when individual nanoparticles can be discerned; conversely, the spongy term refers to those systems in which it is not obvious to isolate individual nanoparticles from the solid matrix. As examples, xerogels usually correspond to corpuscular bodies while zeolites can be classified as spongy materials. A characteristic, which is definitely the basic feature that a real porous network displays (see Fig. 1(a)), is the fact that cavities or chambers (named as *sites*) are surrounded by a number of throats, windows or necks (named as *bonds*) through which the former voids connect to each other. An intuitive property of such a porous network is that cavities always possess larger sizes than their surrounding throats. This idea constitutes the basic *Construction Principle* (CP) that was employed to develop the Dual Site-Bond Model (DSBM) of porous structures [3].

In order to advance theoretically in the visualization of porous networks, sites can be simply assumed as spherical voids which are connected to homologous elements by a number of cylindrical throats (see Fig. 1(b)). In this way, the probability, $S(R_S)$, to choose a site of size R_S or smaller from a certain distribution $F_S(R_S)$ of site sizes expressed on a number-of-elements basis is given by:

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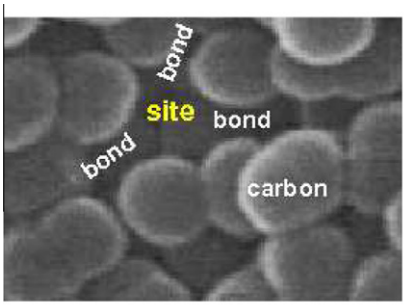
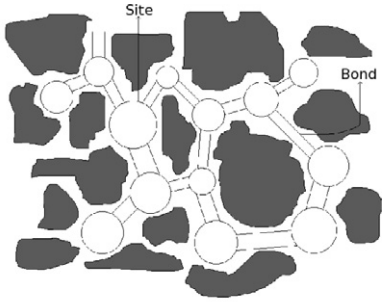


(a) Micrograph of a porous solid made by the random parking of monodisperse carbon microspheres of 146 nm of diameter.



(b) DSBM representation of a porous medium.

Fig. 1. Cavities (sites) and throats (bonds) of porous networks.

$$S(R_S) = \int_0^{R_S} F_S(R_S)dR_S \tag{1}$$

In the same way, the probability, $B(R_B)$ of finding a bond of size R_B or smaller among a given distribution $F_B(R_B)$ of bond sizes is given by:

$$B(R_B) = \int_0^{R_B} F_B(R_B)dR_B \tag{2}$$

Both distributions $F_S(R_S)$ and $F_B(R_B)$ are given on a number-of-elements basis and are normalized according to:

$$\int_0^{\infty} F_S(R_S)dR_S = 1 \tag{3}$$

$$\int_0^{\infty} F_B(R_B)dR_B = 1 \tag{4}$$

An important quantity that determines the topology of a simulated porous medium is the overlap (Ω) between the bond- and the site-size distributions (Fig. 2).

The simulation of porous media requires to consider two laws that are intrinsically comprised within the CP. The first law states that the size of any given site (R_S) must be always larger than (or at least equal to) the size (R_B) of anyone of the C bonds that are delimiting it. In mathematical terms the first law can be written as follows [3]:

$$\textit{First Law} \quad B(R) \geqslant S(R)\ \forall R \tag{5}$$

This last equation implies that the probability of finding a bond of size R or smaller is always greater or at least equal to the probability of finding a site of size R or smaller. This guaranties the existence of a sufficient quantity of bonds of the proper sizes to be connected to sites of size R.

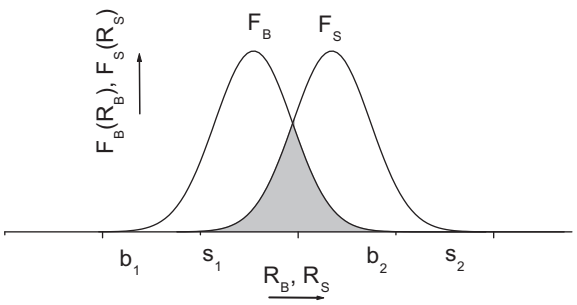


Fig. 2. Overlapping (Ω) between the bond $F_B(R_B)$ and the site $F_S(R_S)$ size distributions. The s_1 and s_2 labels represent the smallest and the largest sites, respectively; similarly, the b_1 and b_2 labels symbolize the smallest and the largest bond entities, respectively.

Now, the interconnection between voids in order to conform a porous network can be summarized by means of the following equations:

- The joint probability, density $\rho(R_S \cap R_B)$, of having a site of size R_S connected to a bond of size R_B is:

$$\rho(R_S \cap R_B) = F_S(R_S)F_B(R_B)\varphi(R_S, R_B) \tag{6}$$

Where $\varphi(R_S, R_B)$ represents the correlation function between the site and bond sizes.

- This site-bond connection has, however, to comply with the CP according to:

$$\textit{Second Law} \quad \varphi(R_S, R_B) = 0\ \forall R_S < R_B \tag{7}$$

This is the mathematical expression of the second law and establishes that the correlation function $\varphi(R_S, R_B)$ is equal to 0 when the size of a bond is larger than the size of the site to which it is connected.

- The correlation function $\varphi(R_S, R_B)$ of a site R_S, connected to a bond of size R_B, if only $R_S \geqslant R_B$ is given by:

$$\varphi(R_S, R_B) = \frac{exp\left(-\int_{S(R_B)}^{S(R_S)} \frac{dS}{B-S}\right)}{B(R_S) - S(R_S)} = \frac{exp\left(-\int_{B(R_B)}^{B(R_S)} \frac{dB}{B-S}\right)}{B(R_B) - S(R_B)} \tag{8}$$

The two simple laws mentioned above allow the construction of porous networks according to the DSBM. Fig. 3 shows a graphical example of a 2-D porous network of varying connectivity where the CP is fulfilled.

2. A Biased Simulation Early Design (BiaSED) method for the construction of pore networks via the DSBM

A complete account of the method that was previously employed to simulate pore networks through the DSBM can be found in reference [4]; a brief description of this method is as follows. Heterogeneous (in size) 3-D cubic porous networks were built by a Monte Carlo method on the basis of the DSBM [5]. The desired topological properties of the simulated substrates were introduced by considering a variety of sizes of sites and bonds. The connectivity (i.e. the number of bonds that surround and connect the sites with their homologous entities) was kept constant. No geometrical restrictions, in the sense that the bonds that meet into a site were not physically interfering with each other, were regarded in this work. Under the above premises, we presented a Monte Carlo (MC) method [5] for the construction of porous networks endowed with size correlations between pore entities. First, a cubic three dimensional network of size $L = N \times N \times N$ sites interconnected