Determination of the pore size distribution of correlated mesoporous networks

R. H. López, A. M. Vidales, G. Zgrablich

Abstract In the present work we study how the adsorption desorption hysteresis loop of a mesoporous disordered medium represented by a 3-dimensional Dual Site-Bond Model (DSBM) is affected by percolation. Site and bond distributions are assumed to be gaussians. The behavior of the threshold pressure for the evaporation processe suggests a method to determine the site and bond distributions from experimental adsorption-desorption hysteresis curves. Traditional methods developed for non-correlated networks are tested and evaluated against our simulation results showing the discrepancy mainly for highly correlated networks. Results of the prediction capability of our method are shown.

Keywords Porous media, porous networks, Monte Carlo

1
Introduction

The characterization of mesoporous materials, specially regarding the determination of the pore size distribution, from adsorption-desorption experiments is a subject of great practical importance and still stands as an open problem presenting interesting theoretical challenges [1–7], and this is more remarkable in the case of disordered (or amorphous) porous media. In fact, the shape and extent of the adsorption-desorption hysteresis loop (ADHL) of vapors in mesoporous materials are known to be influenced by several characteristics of the porous space; the geometrical shape of the pores, their size distribution and the interconnectivity of the porous network are among those which have been studied intensively for a long time. The problem has two aspects: in first place, a model describing the properties of the medium must be given, and then, within that model, a procedure to determine the pore size distribution must be developed. Modeling of porous media has evolved along two different, but complementary, lines: continuum and discrete models. Continuum models, based on a continuous characteristic function, attaining the value 0 at an empty point and 1 at a solid point, has proven to be more adequate to study the flux of fluids through the medium [8–12]. On the other hand, discrete models, representing the porous space by a network of voids (sites) connected by throats (bonds), have demonstrated to be a powerful tool to study the percolation properties of the medium and those phenomena depending on its topological properties [2, 4, 5, 7, 13–15]. Among the family of discrete models, the Dual Site-Bond Model (DSBM), introduced by Mayagoitia et al. [2] is the simplest model which takes into account spatial correlation among pore sizes, allowing in this way to generate porous networks with different structures. Within the framework of this model, through analytical calculations on a Cayley tree (where no closed loops are involved) [13] and through Monte Carlo simulations in two-dimensional networks [14], it has been shown that spatial correlation among pore sizes affect drastically percolation probabilities. It is then to be expected that in more realistic three-dimensional networks spatial correlation will have similar effects on the percolation probabilities and these, in turn will affect the ADHL. Accordingly, the first, and central, purpose of this work is to study how the ADHL is influenced by spatial correlation as described by the DSBM. The problem of obtaining the site and bond size distributions from the analysis of ADHL has been solved so far only for non-correlated porous networks and in the extreme cases where the pore volume can be attributed either entirely to the sites or entirely to the bonds [5, 16, 17]. It seems that the hypothesis that the main pore volume resides in the sites, while the bonds only play a role in the interconnectivity effects is reasonable for a variety of porous solids [5] and, in order to keep the present study simple with respect to all aspects which are irrelevant to our central purpose, it will be assumed in what follows. Our second purpose in this work is to take a first step toward the development of a method to determine the site and bond size distributions from the analysis of ADHL, for the general case of correlated porous networks.

2
Dual Site-Bond Model (DSBM)

Let $S(R)$ and $B(R)$ be the distribution functions associated with the site and bond size R, and $F_S(R)$ and $F_B(R)$ the corresponding probability density functions, such that

$$S(R) = \int_0^R F_S(R)dR, \qquad B(R) = \int_0^R F_B(R)dR, \qquad (1)$$

and let the intervals $s = [s_1, s_2)$ and $b = [b_1, b_2)$ be the support of site and bond measures, i.e., the set of values of R for which F_S and F_B are positively defined. The way

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in which sites and bonds are connected to form the network is given by the joint probability density function, $F(R_S, R_B)$, of finding a site with size $R_S \epsilon (R_S, R_S + dR_S)$ connected to a bond with size $R_B \epsilon (R_B, R_B + dR_B)$. The two basic laws describing the DSBM are:

$$B(R) - S(R) \geq 0 \tag{2}$$

$$F(R_S, R_B) = 0 \quad for \quad R_S < R_B \tag{3}$$

The first law, Eq. (2) implies that $b_1 \leq s_1$ and $b_2 \leq s_2$, while the second law, Eq. (3), called the *Construction Principle* (CP), is of a local nature and expresses the fact that the size R_B of any bond cannot be bigger than that of the two connected sites (in a porous medium the size of a throat cannot be larger than that of the two connected voids). If the joint probability function is expressed as

$$F(R_S, R_B) = F_S(R_S) F_B(R_B) \Phi(R_S, R_B) \tag{4}$$

then the correlation function Φ carries the information about the site-bond assignation procedure in the network. In the simplest case where sites and bonds are assigned to each other in the most random way as allowed by the CP, called the Self Consistent case, then $\Phi(R_S, R_B)$ attains the following expression:

$$\Phi(R_S, R_B) = \frac{exp[- \int_{R_B}^{R_S} dB/(B - S)]}{B(R_B) - S(R_B)} \tag{5}$$

If we denote by Ω the overlapping area between the site and bond probability density functions, the function Φ has the following properties: (i) $\Phi_{\Omega \to 0}(R_S, R_B) = 1 \forall R_S, R_B$, meaning that in this limit sites and bonds are distributed completely at random, and (ii) $\Phi_{\Omega \to 1}(R_S, R_B) \propto \delta(R_S - R_B) \forall R_S, R_B$, sites and bonds group together in macroscopic patches, each having a value of R. Then, the overlapping Ω is the fundamental parameter describing the topology of the network in this model. This behavior also suggests that Ω must be related to some *correlation length* (which would be a physically more meaningful parameter), characteristic of the decay of the spatial correlation function defined as:

$$C(r) = \langle R_S(\vec{r}_0) R_S(\vec{r}_0 + \vec{r}) \rangle = \langle R_B(\vec{r}_0) R_B(\vec{r}_0 + \vec{r}) \rangle \tag{6}$$

In fact, it is expected that $C(r)$ decays approximately in an exponential form (this would be the exact behavior for a one-dimensional network generated by a Markov chain of events):

$$C(r) = exp(-r/l_0) \tag{7}$$

where l_0 is the correlation length (measured in lattice constants). This expression has been used extensively in applications of the DSBM [7,21] together with the ansatz

$$l_0 = \frac{\Omega}{1 - \Omega} \tag{8}$$

relating the overlapping with the correlation length, in such a way that $l_0 \to 0$ for $\Omega \to 0$ and $l_0 \to \infty$ for $\Omega \to 1$. The problem of the generation of DSBM networks has been intensively investigated [2,7,18,20]. We employ here the method presented in [7,19] for the Monte Carlo generation of such networks, which can be resumed in the

following very simple terms. An initial network is prepared by sampling the values of R_S and R_B from the corresponding probability density functions F_S and F_B and distributing them completely at random on the lattice. This network will have the correct F_S and F_B but not the correct $\Phi(R_S, R_B)$, in particular the CP is not obeyed everywhere. Then a Markov chain of new states of the network is generated by choosing at random pairs of sites (or bonds) attempting to exchange them, the exchange is accepted if it does not violate the CP. It has been demonstrated [19] that this procedure leads finally to the equilibrium distribution for the network and that it does not suffer of the imperfections introduced by other methods (mainly anisotropy).

3
Adsorption-desorption process
3.1
Theoretical background

The study of mesoporous solids is closely related to the concept of capillary condensation and its quantitative expression given by the Kelvin equation. A convenient form to the Kelvin equation is:

$$ln(P/P_0) = \frac{-2\gamma V_L}{R_m RT} \tag{9}$$

where P/P_0 is the relative pressure of the vapor in equilibrium with a meniscus having a radius of curvature R_m. P_0 is the saturation vapor pressure corresponding to $R_m = \infty$, γ is the surface tension, and V_L is the molar volume of the liquid. In applying Eq. (9), one must take into account that during capillary condensation the pore walls are already covered with an adsorbed film of thickness t_a. Thus, capillary condensation actually occurs not directly in the pore but rather in the inner core, and we have the followings connections between R_p (pore radius) and R_m:

$$R_p = R_m + t_a \tag{10}$$

(The last Eq. is obtained assuming that the angle of contact between the liquid and the solid surface is $\theta = 0$). The thickness of the adsorbed film can be estimated using a multilayer adsorption isotherm, such as that given by Halsey equation [22], which for nitrogen is written as:

$$t_a = 3.54 \left[\frac{5}{ln(P_0/P)} \right]^{1/3} \tag{11}$$

3.2
Description of adsorption

The pore space can generally be treated as a lattice of voids interconnected by necks in a three-dimensional network. It is often possible to consider that the pore volume is concentrated in void, whereas necks do not possess a volume of their own. In the framework of this model, the filling of every void on the adsorption branch of the isotherm is determined only by the individual void characteristic and does not depend on the neck-size distribution. In particular, voids with radii lower than the Kelvin radius,
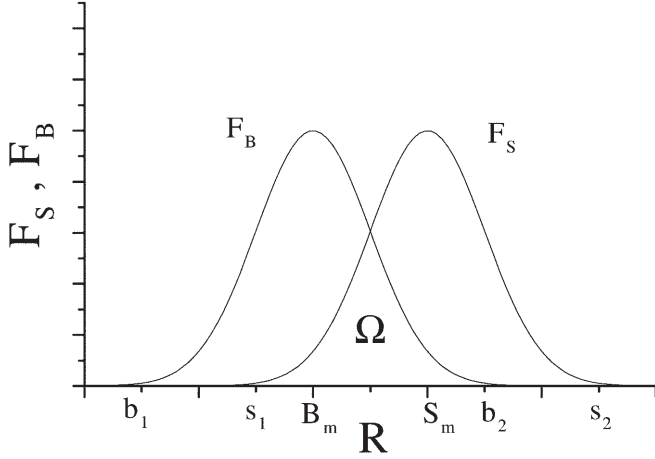
Fig. 1. Gaussian probability density functions for sites and bonds used to simulate the network

$R < R_p$, are completely filled and those with $R > R_p$ are filled only partly via reversible sorption mechanism (multilayer adsorption). A differential analysis of the adsorption branch of the isotherm allows then the determination of the void-size distribution (site distributions).

3.3
Description of desorption

The desorption process is dependent both on the void (pore) and neck (bond) size distributions, $F_b(R)$ and $F_s(R)$. If the radii of all the voids are larger than those of all the necks (i.e., $s_1 > b_1$); (Fig. 1) and the void and neck arrangements are random, the desorption process is mathematically equivalent to the bond problem in percolation theory. In practice, the case in which the size distributions of voids and necks do not overlap ir rare. In general, these distributions may be overlapping, introducing correlations in the arrangement of voids and necks. For the desorption stage, a pore (site or bond), having the appropriate radius ($R > R_p$), evaporates only if it is connected to the vapor phase by a continuous path of already evaporated pores. This last condition introduces cooperative effects in the desorption branch which can be expressed by the relation:

$$[1 - V_{des}(R_p)] = [1 - V_{ad}(R_p)]P_b(Z_q) \qquad (12)$$

where $V_{ad}(V_{des})$ is the volume filled with adsorbate in the adsorption (desorption) branch, q is the fraction of bonds with $R > R_p$, P_b is the percolation probability for the bond problem and Z is the mean cordenation number for voids with $R > R_p$. This percolation factor produces an inhibiting effect during the evaporation process: the larger is the percolation threshold the greater will be the retarding on the evaporation branch.

4
Determination of bond size distribution from experimental adsorption-desorption hysteresis curves

Zhdanov et al. [23,5] propose a method to calculate the bond size distribution from experimental adsorption desorption hysteresis curves. This method take into account

only the simplest effect, i.e., the fact that the neck between the two nearest-neighbor void should be lower than or equal to the size of the smaller void, but it does not take into account spatial correlations induced by the Construction Principle. This method assumes that the percolation probability for the sublattice of voids with $R > R_p$ is the same as the universal percolation probability for the bond problem given by Kirkpatrick:

$$P_b(x) = \begin{cases} 0 & \text{if } x < 1.5 \\ \frac{1.54(x-1.5)^{0.4}}{[1+0.606(x-1.5)^{0.4}]} & \text{if } 1.5 \leq x \leq 2.7 \\ 1 & \text{if } x > 2.7 \end{cases}$$

The parameter $x(Zq)$ can be obtained neglecting correlations as:

$$Zq = z_0\Phi(R_p)/\psi(R_p) \qquad (13)$$

where z_0, the mean overall connectivity, can be obtained through Seaton's method; and:

$$\Phi(R) = \frac{\int_{R_p}^{b_2} F_b(R)dR}{\int_{b_1}^{b_2} F_b(R)dR}, \qquad \psi(R) = \frac{\int_{R_p}^{s_2} F_s(R)dR}{\int_{s_1}^{s_2} F_s(R)dR}, \qquad (14)$$

From the hysteresis curve, P_b can be obtained for a given $R - p$. Then, from Kirkpatrick Eq. the corresponding value of $x = Zq$ is determined and finally, since F_s is known, $F_b(R_p)$ is obtained from Eq. (13).

5
Simulation

Cubic porous networks of $LxLxL$ (it was determined that finite size effects became negligible for $L = 50$, so that this was the size finally used to obtain our results) are generated sampling the sites and bonds radii from two truncated and renormalized gaussian distributions, with mean values S_m and B_m, respectively, and the same standard deviation σ. The limits for sampling radii for sites and bonds were chosen to be $S_m \pm 2\sigma$ and $B_m \pm 2\sigma$ respectively. Samples with different overlapping Ω, and then with different correlation length l_0, were generated by moving the bond distribution while keeping the site distribution fixed. Once the desired porous network is simulated, sorption isotherms are simulated, recording the adsorbed or desorbed volume V as a function of p_0/p.

6
Results and discussion

Series of ADHL were obtained for site and bond gaussian distributions with σ=1, 2.5, 5; S_m=75, 100, 125 and B_m ranging from 30 to S_m(all size and distances units are in Angstrom). In Fig. 2, the behavior of ADHL as S_m changes, when σ and d are fixed, can be observed. The adsorption branch, and consequently the whole ADHL, moves to higher relative pressure as Sm increases, as expected. The desorption branch presents a well defined knee, whose position should be in close correspondence with the percolation threshold, according to Eq. (12). From the above it turns out that the position of the desorption knee, which we denote as P^*, is a relevant parameters to describe the
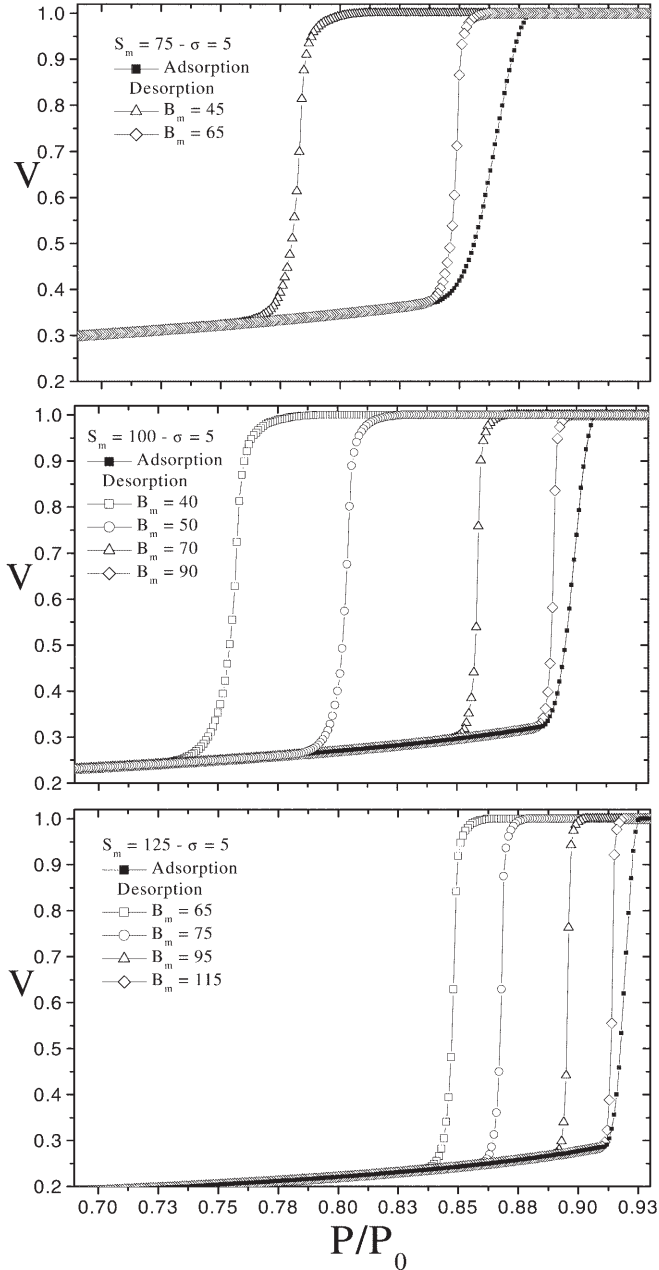
Fig. 2. ADHL for fixed σ and S_m and for different values of B_m

Fig. 3. Plot of all simulation results (symbols) against P^* and fitted curve (full line) corresponding to Eq. (15)

Fig. 4. Comparation between Zhdanov method and our method against simulated hysteresis curves

behavior of ADHL. Of course, the exact values of this parameter depend on the way in which this relative pressure is determined from the ADHL, and this could be quite arbitrary. Just to fix a simple criterion, we take as P^* the value of the relative pressure where the normalized adsorbed volume takes the value 0.9 on the desorption branch. With this we obtain the variation of B_m with P^*, for different values of S_m and σ, shown in Fig. 3. All results can be approximated by the curve:

$$B_m = \frac{1}{0.1 - 0.1P^*} \tag{15}$$

This curve can be used as the basis of a first approximation method to estimate the site and bond size distributions from experimental ADHL, assuming that these distribu-
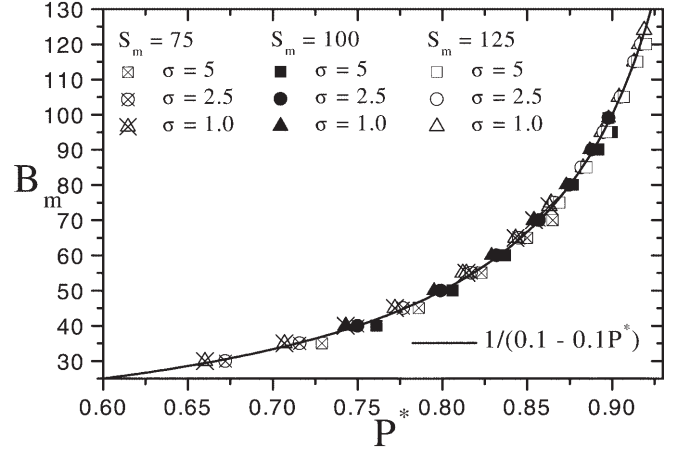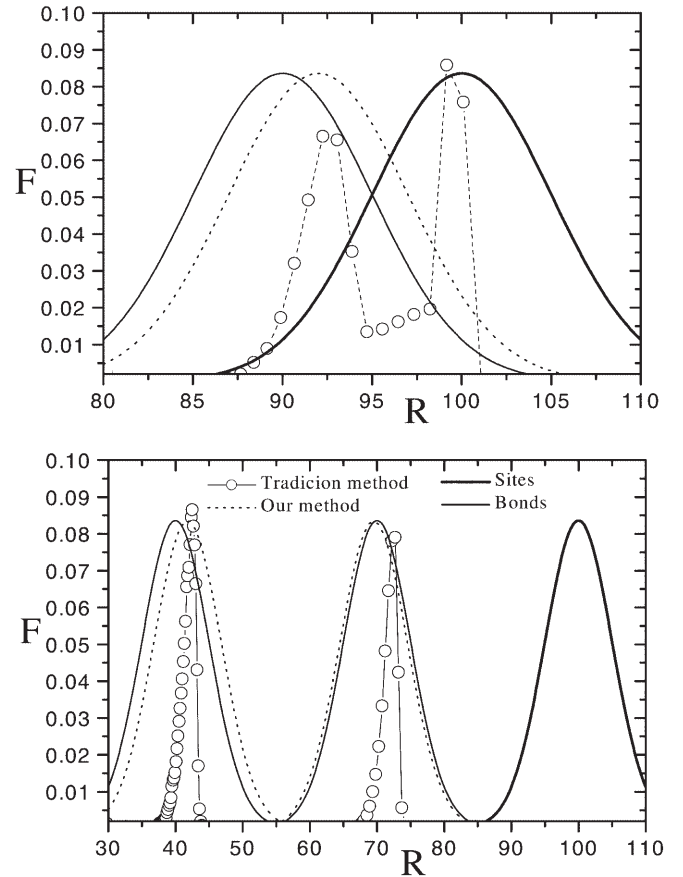
tions would have a definite shape (in this case gaussian, but the method can be worked out for other distributions, for example lognormal). In fact, since no percolation effects are present for the adsorption branch, a differential analysis of the experimental adsorption curve yields the site distribution [1] and, consequently, S_m and σ. Moreover, from the experimental ADHL, P^* can be determined and replacing this value in Eq. (15) the value of B_m, is obtained and the bond distribution is thus determined. Of

course, a finer determination of B_m could be obtained by using the value of P^* in the curve corresponding to the actual values of S_m and σ. In the Fig. 4 we tested numerically this method and the method given by Zhdanov against simulated hysteresis curves.

7
Conclusions and perspectives

The DSBM is the simplest available model to take into account correlations. Based on the DSBM we proposed a simple characterization method from experimental adsorption desorption hysteresis, a technique accessible to any laboratory. Improvements to this method could result from the study of the effects of correlations on percolation probabilities in 3D. Refinements to the model can be introduced by considering additional correlations, beyond those induced by the Construction Principle.

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