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Abstract. The capillary hysteresis for the drainage–imbibition process in correlated site–bond porous networks is studied. The degree of correlations between pore radii is shown to produce important modifications on the hysteresis loop which is wider for non-correlated networks and narrower for correlated ones. A relation between the degree of correlation and the type of solid is suggested.

1. Introduction

The behaviour of fluids on heterogeneous porous media is a subject of great interest for science and engineering. Flow phenomena in natural and synthetic porous materials, and their connection with the most sophisticated techniques of statistical physics of disordered media (fractals, percolation, scaling laws, etc), has been recently reviewed by Sahimi [1].

In this work we study the capillary hysteresis loops that various porous materials offer during the drainage and imbibition processes, where a non-wetting phase displaces a wetting one and vice versa. In this kind of process, in which a liquid enters and leaves a pore space, two main characteristics are observed: a percolation threshold and a hysteresis loop [2, 3]. These characteristics can be explained by considering the pore space to fill and empty in discrete steps which involve network connections to particular phases, i.e., it is necessary to take into account the network topology. The simplest model for capillary hysteresis considers the porous media as a network of channels obeying capillary laws. In a porous medium, however, the pore space can be divided into two classes: pore bodies, where most of the porosity resides, and pore throats, which are the channels that connect the pore bodies. In a network representation of the pore space, the pore bodies are equivalent to the sites of the network, and the pore throats are equivalent to its bonds. The fluid penetration will only be possible when a critical fraction of sites and bonds are opened, i.e., they fulfil capillary law requirements for invasion. The site–bond percolation problem and its application to capillary hysteresis in a porous network has already been investigated by Yanuka [4]. However this author did not treat the most general case where a correlated network is considered. It has already been shown [5] that the degree of correlation in those networks strongly affects the shape of hysteresis loops for nitrogen sorption and mercury porosimetry. In the present work we intend to study the effect of correlations between pore radii in a site–bond porous network on the capillary hysteresis for a drainage–imbibition process.

2. Site–bond description of porous media

We consider a porous solid as a three-dimensional network of $N(N \rightarrow \infty)$ sites (or voids) connected by bonds (or throats); figure 1. The number of bonds emerging from a given site is the connectivity z of that site. We suppose that site and bond sizes are statistically distributed by frequency functions, $F_s(R)$ and $F_b(R)$, respectively, such that $F_s(R)\,dR(F_b(R)\,dR)$ is the probability of finding a site (bond) with radius between R and $R + dR$. The site and bond distribution functions, $S(R)$ and $B(R)$, given by

$$S(R) = \int_0^R F_s(R)\,dR \qquad B(R) = \int_0^R F_b(R)\,dR \qquad (1)$$

represent the probability of finding a site or a bond, respectively, with a radius no greater than R.
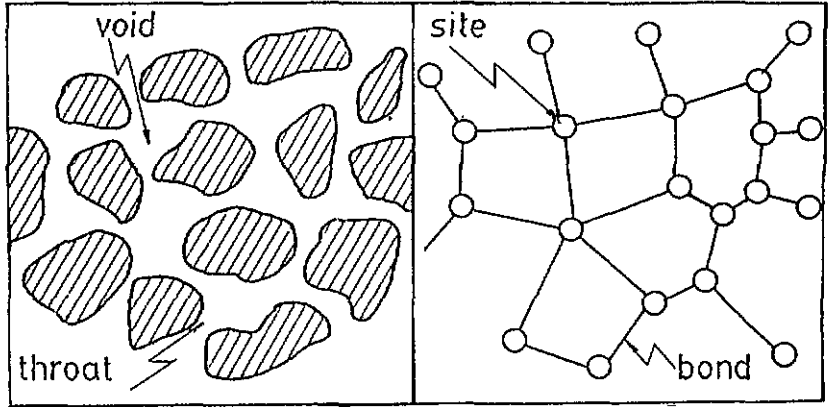

Figure 1. Porous space of voids and throats and its schematic representation as a network of sites and bonds.

In order to build the site–bond network, we adopt the following rule: for every site, its *size is always greater than, or at least equal to, the size of any of its z bonds*. Then it is necessary that all the bonds have sizes sufficiently small, such that

$$B(R) \geqslant S(R) \qquad \text{for every } R. \qquad (2)$$

Overlap between the frequency curves is allowed, figure 2, meaning that there will be some bonds of size greater than some sites. The fact that sites and bonds cannot be randomly interconnected is then taken into account by assuming that the site–bond connected pairs are statistically described by the joint distribution function

$$F(R_s, R_b) = F_s(R_s)F_b(R_b)\phi(R_s, R_b) \qquad (3)$$

where $F(R_s, R_b)\,dR_s\,dR_b$ is the probability of finding a site with size between R_s and $R_s + dR_s$, connected to a bond with size between R_b and $R_b + dR_b$; and $\phi(R_s, R_b)$ is a correlation function characterizing the porous medium. If $\phi = 1$, the events of finding a site of size R_s connected to a bond of size R_b would be independent and the network would
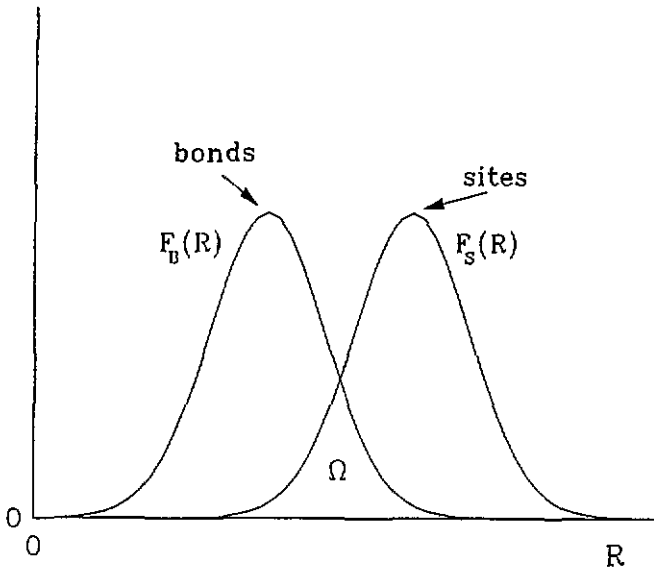
Figure 2. Dual size distributions, one for bonds and one for sites, with an overlap area Ω between them.

be built randomly. Then, the fact that a bond of size R_b cannot be connected to a site of size $R_s < R_b$ is expressed as

$$\phi(R_s, R_b) = 0 \qquad \text{for } R_s < R_b. \tag{4}$$

An expression for the correlation function can be obtained by assuming a method of generation of what are the fundamental building blocks of the network, i.e., a site with its two bonds, which will build up the complete network once they are brought together. The simplest form of $\phi(R_s, R_b)$, which we shall use here, is the one that allows the maximum degree of randomness compatible with the construction rule, and is given by [6–8]

$$\phi(R_s, R_b) = \begin{cases} \left(\exp\left[-\int_{S(R_b)}^{S(R_s)} \frac{dS}{B-S} \right] \right) \Big/ [B(R_s) - S(R_s)] & \text{for } R_s \geqslant R_b \\ 0 & \text{for } R_s < R_b \end{cases} \tag{5}$$

with these limiting values

$$\lim_{\Omega \to 1} \phi(R_s, R_b) = \frac{\delta(R_s - R_b)}{F_s(R_s)} \tag{6}$$

$$\lim_{\Omega \to 0} \phi(R_s, R_b) = 1 \tag{7}$$

where Ω is the overlap common area between $F_s(R_s)$ and $F_b(R_b)$ and δ is the Dirac delta function.

In the simplest case where sites and bonds are uniformly distributed

$$F_s(R) = \begin{cases} F_0 & \text{for } s_1 \leqslant R \leqslant s_2 \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

$$F_b(R) = \begin{cases} F_0 & \text{for } b_1 \leqslant R \leqslant b_2 \\ 0 & \text{otherwise} \end{cases} \tag{9}$$

where $s_2 - s_1 = b_2 - b_1 = 1/F_0$; the correlation function takes the form

$$\phi(R_s, R_b) = \frac{1}{1 - \Omega} \exp[-\alpha(R_s, R_b)\Omega/(1 - \Omega)] \tag{10}$$

where α is a piecewise function given by

$$\alpha(R_s, R_b) = \begin{cases} (R_s - s_1)/(b_2 - s_1) & \text{for } R_b \leqslant s_1, R_s \leqslant b_2 \\ 1 & \text{for } R_b \leqslant s_1, R_s > b_2 \\ (R_s - R_b)/(b_2 - s_1) & \text{for } R_b > s_1, R_s \leqslant b_2 \\ (b_2 - R_b)/(b_2 - s_1) & \text{for } R_b > s_1, R_s > b_2 \end{cases} \tag{11}$$

and Ω is the overlap between $F_s(R)$ and $F_b(R)$.

The topography of the pore space strongly depends on the overlap degree Ω. With $\Omega = 0$, we have an uncorrelated porous structure where sites and bonds are very well differentiated entities randomly assigned to each other. For $\Omega \sim 1$ we have the opposite case, namely a very correlated structure where bonds connected to a given site have almost the same radius as that of the site. In practice, the structure can be considered as a collection of macroscopic domains of uniform pore sizes. In an intermediate situation between these two extremes, we find a variety of interconnected pore sizes (a given site can be connected to bonds ranging from very small sizes 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 natural porous media.

It is to be expected that these different porous structures will present different percolation behaviours and also different characteristics in their capillary hysteresis loops, and this will be shown in the following sections. In what follows we shall assume that the pore volume is predominantly associated with sites. The treatment can be easily extended to the case where the pore volume is associated to bonds or to both.

3. Percolation probabilities in a correlated network

In this section we present the relation between pore structures and their percolation properties. The classical application of percolation theory to model pore networks is the random site–bond percolation problem, in which both sites and bonds in a lattice are randomly occupied or open. The open or closed states of sites and bonds will depend upon the physical process to be considered. In capillary phenomena these states can be obtained from Laplace's equation. The following definition seems suitable: a site (bond) is considered to be opened if its radius is greater than some critical radius c_s (c_b). The critical radii c_s and c_b may be different since they depend on the pore geometry. If the site and bond distribution functions, $F_s(R)$ and $F_b(R)$, have a common area, we must use correlated site–bond percolation to model capillary processes, because the state of any element (site or bond) will be subject to the state of its neighbouring elements. The main problem is now to calculate the percolation probabilities for a given correlated site–bond network. The site (bond) percolation probability $P^s(P^b)$ is the probability that any open site (bond) belongs to the infinite cluster of open elements. A cluster of all open elements is said to be infinite if it spans the network.

We shall give here briefly the solution for the percolation problem in a correlated site–bond Bethe lattice of coordination number z, figure 3, in which the correlation function

is given by $\phi(R_s, R_b)$. The employment of these types of lattice is suitable, since this will allow an approximate analytical solution and a description of percolation probabilities qualitatively valid for other lattices. If $c_s(c_b)$ is the site (bond) critical radius, then the probability for a site (bond) to be opened, $p_s(p_b)$, is given by

$$p_s = \int_{c_s}^{\infty} F_s(R) \, dR \tag{12}$$

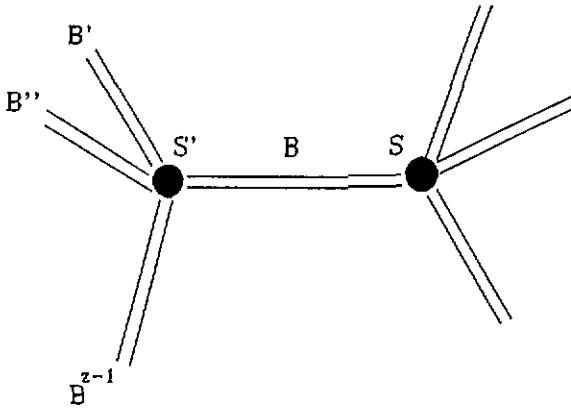$$p_b = \int_{c_b}^{\infty} F_b(R) \, dR. \tag{13}$$

Figure 3. The Bethe lattice of coordination number z.

Let us introduce the following probabilities for the multiple events; figure 3: p_{sb} = probability for the event *site S and bond B both open*. $p_{s\bar{b}}$ = probability for the event *site S open and bond B blocked*. $p_{sbs'}$ = probability for the event *site S, bond B, and site S' all open*. $p_{sb\bar{s}'}$ = probability for the event *site S and bond B open, site S' blocked*. $p_{bsb'}$ = probability for the event *bond B, site S and bond B' all open*. $p_{bs\bar{b}'}$ = probability for the event *bond B and site S open, bond B' blocked* and so on for greater clusters. All these probabilities are calculable in terms of p_s, p_b and Ω in the case of the uniform distribution; for example

$$p_{sb} = \int_{c_s}^{s_2} dR_s \int_{c_b}^{R_s} dR_b \, F_s(R_s) F_b(R_b) \phi(R_s, R_b) \tag{14}$$

$$p_{sbs'} = \int_{c_s}^{s_2} dR_s \int_{c_s}^{s_2} dR_{s'} \int_{c_b}^{\min[R_s, R_{s'}]} dR_b \, F_s(R_s) F_b(R_b) F_s(R_{s'}) \phi(R_s, R_b) \phi(R_{s'}, R_b). \tag{15}$$

To obtain the percolation probabilities for a Bethe lattice of connectivity z, we follow the method introduced by Essam for random percolation [9], and generalized by Coniglio for the percolation of interacting spins [10]. Let $Q_s(Q_b)$ be the probability that a branch starting from an open site (bond) becomes blocked somewhere. Then the site and bond percolation probabilities can be obtained through

$$P^s = 1 - Q_s^z \tag{16}$$

$$P^b = 1 - Q_b^2 \tag{17}$$

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

$$Q_s = \frac{p_{s\bar{b}}}{p_s} + \frac{p_{sb\bar{s}'}}{p_s} + \frac{p_{sbs'}}{p_s} Q_s^{z-1} \tag{18}$$

$$Q_b = \frac{p_{b\bar{s}}}{p_b} + \frac{p_{bs}}{p_b} \left[\frac{p_{bs\bar{b}'}}{p_{bs}} + \frac{p_{bsb'}}{p_{bs}} Q_b \right]^{z-1}. \tag{19}$$

This allows the calculation of site and bond percolation probabilities, P^s and P^b, and the percolation thresholds, as functions of p_s, p_b and Ω. The details for solving the equations (18) and (19) in the general correlated case $\Omega \neq 0$ are given in [11]; here we only present the main results for a site–bond Bethe lattice of connectivity $z = 3$. The behaviours of the percolation probabilities P^s and P^b as functions of p_s at $p_b =$ constant, in the simple case of uniform site and bond distributions, are given in figure 4. We see that the percolation probabilities are very sensitive to the overlap degree Ω, and that high values of Ω make the percolation threshold decrease. Thus the correlations of the porous structure facilitate the percolation. These results for the correlated site–bond Bethe lattices are qualitatively identical to that obtained by numerical simulation on the correlated site–bond square lattice [12]. We shall see that the characterization of the porous structures by the dual site–bond distribution is adequate and that the observed behaviour of P^s and P^b gives a consistent picture of the general characteristics of capillary hysteresis loops for a great variety of agglomerated materials.
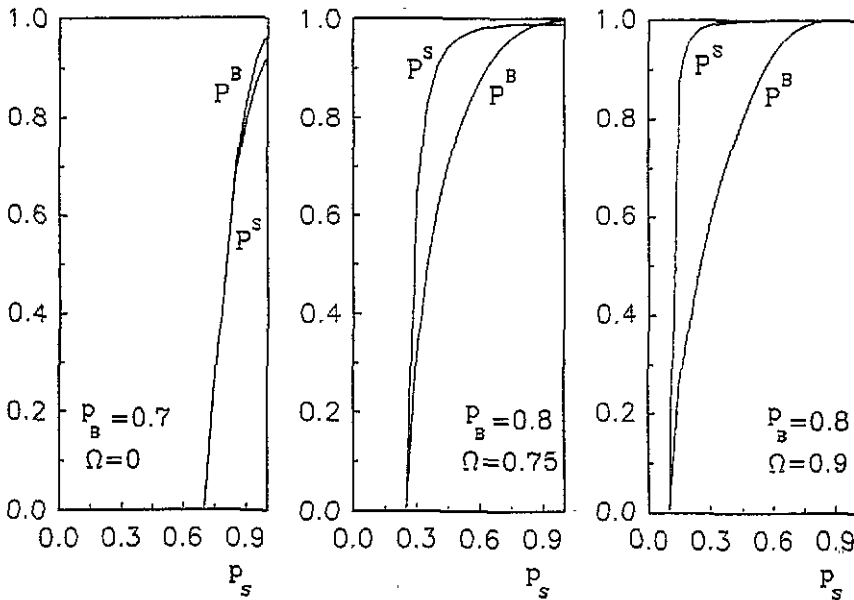

Figure 4. Site and bond percolation probabilities, P^s and P^b, on the Bethe lattice with $z = 3$, as functions of p_s (fraction of open sites), for different constant values of Ω and p_b (fraction of open bonds).

4. Drainage–imbibition process

The equation governing the drainage–imbibition process is the Laplace equation for capillarity:

$$\mathcal{P} = 2\sigma/R_{\mathrm{m}} \tag{20}$$

where $\mathcal{P}$ is the capillary pressure developed across the interface between the wetting and the non-wetting phase in the pore space, σ is the interfacial tension, and $1/R_{\mathrm{m}}$ is the average curvature of the interface. This equation determines whether a site or a bond is opened or not to the fluid flow. For a given external pressure some of the pores in the porous medium will be 'open', i.e., will let fluid flow through them in relation to their sizes, and others will be 'closed', i.e., will have a size such that they will not permit fluid flow.

In the drainage process the smallest pores determine the pressure at which the pore will drain. On the other hand, during imbibition, the largest pores determine the pressure at which the pore will fill. The pressure difference in emptying or filling the pores is one of the major reasons for capillary hysteresis phenomena in these media and in this work it will be considered the only one.

From the preceding analysis we may deduce that the drainage process will take place in pores for which the external pressure exceeds the critical value of the pressure at the pore throat level, i.e., we may associate this process to a bond percolation problem. During imbibition, on the other hand, the pore will fill entirely if the external pressure is lower than a critical value at the pore body level and we may associate this process to a site percolation problem. If S_{w} is the saturation fraction of the wetting phase for a solid at a given external pressure $\mathcal{P}$, $p_s(p_b)$ the fraction of sites (bonds) whose radii fulfil the Laplace equation corresponding to that pressure, and $V^+(V^-)$ the volume fraction belonging to sites whose radii are greater (lower) than the critical Laplace radius, r_L, then for the drainage process

$$S_{\mathrm{w}} = 1 - P^b(p_s, p_b)V^+(r_L) \tag{21}$$

and for the imbibition process

$$S_{\mathrm{w}} = P^s(1 - p_s, 1 - p_b)V^-(r_L) \tag{22}$$

where $P^s(P^b)$ are the site and bond percolation probabilities in the Bethe lattice. This accounts for capillary hysteresis without the trapping effect.

5. Results and discussion

The calculated percolation probabilities P^s and P^b for different degrees of the overlap Ω are introduced in (21) and (22) to obtain the corresponding hysteresis loops in figure 5. There we show the network saturation fraction, S_{w}, of the wetting phase against $1/R_{\mathrm{m}}$ that is proportional to the pressure developed at the interface.

We observe that, during drainage, S_{w} is equal to unity until a critical value in the pressure is attained. This value corresponds to the radius at which the minimum necessary fraction of 'opened' bonds is allowed. At these stages the so-called breakthrough pressure is reached, and sites may drain.
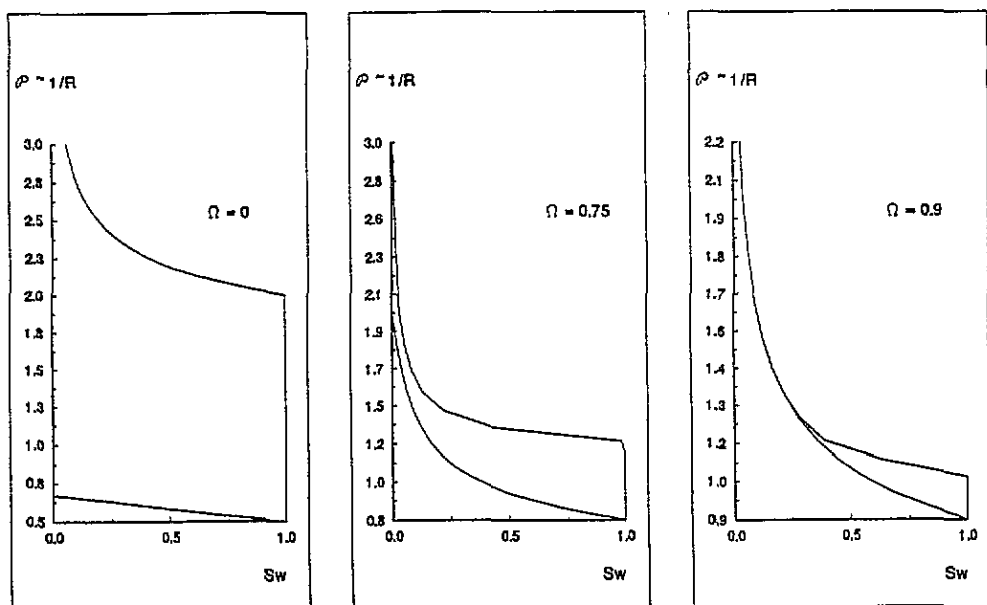
Figure 5. Numerical results for drainage (upper) and imbibition (lower) in correlated site–bond Bethe networks, showing the hysteresis loops for three different values of the overlap Ω.

On the other hand, during imbibition, bonds must wait the critical condition for sites, i.e., the minimum necessary fraction of 'opened' sites that permits imbibition. The plateau on the curves indicates the breakthrough pressures for which drainage and imbibition begin.

As the overlapping between the two size distributions increases the percolation thresholds decrease and the critical conditions are more rapidly fulfilled, then the breakthrough pressures are overtaken at lower values (figure 5).

If we keep in mind the relation between the two critical conditions mentioned and the overlap, we realise that these conditions are much the same at very high overlap, meaning that we could not have any hysteresis loop because the two curves would coincide. For lower degree of the overlap, these two critical conditions are more and more separated, and in the limiting case $\Omega = 0$, all sites must 'wait' until the critical condition for bonds is achieved during drainage (random bond percolation), and vice versa during imbibition (random site percolation), then a wide hysteresis loop just like that in figure 5 is obtained.

One way of producing porous materials is through the agglomeration of particles with different shapes. The resulting pore structure will depend on the packing efficacy of the constituent particles, which is a function of their symmetry properties [13–15].

The packing of spherical particles creates a porous network in which pore bodies and pore throats are very well differentiated entities. Obviously, such a structure should be represented by a site–bond distribution with an overlap degree $\Omega = 0$. Almost the same occurs if the constituent spheres are not perfectly homogeneous. According to the percolative properties of this type of structure, the percolation threshold is maximum and a wide hysteresis loop like the one shown in figure 5 for $\Omega = 0$ is expected.

A very different behaviour occurs for the packing of platelike particles. These particles, with only one symmetry axis, tend to pack by aligning themselves face to face creating little differences between the sizes of bodies and throats. We then expect for this kind of structure a site–bond distribution with a very high overlap degree Ω. This means that

the percolation threshold is quite low, so the breakthrough pressure, and a much narrower hysteresis loop than that corresponding to spheres would be observed. It is worth remarking that the imbibition branch is a little steeper than the drainage one, according to the difference between P^s and P^b for high values of Ω.

We see then that agglomerates of particles of different shapes, due to their particular packing efficiency, form different porous structures that can be reasonably characterized by the site–bond joint distributions. This characterization, due to the percolation properties of correlated site–bond networks, is able to predict porosimetric and sorption loops that are at least qualitatively consistent with the observed experimental behaviour of many carefully controlled samples [5, 16].

In conclusion, the joint site–bond description of porous structures, together with the percolation model for correlated site–bond networks, seems to be appropriate to characterize more completely complex porous materials occurring in nature.

References

[1] Sahimi M 1993 *Rev. Mod. Phys.* **65** 1393
[2] Mason G 1988 *Characterization of Porous Solids* ed K K Unger *et al* (Amsterdam: Elsevier)
[3] Mason G 1988 *Proc. R. Soc.* A **415** 453
[4] Yanuka M 1990 *J. Colloid Interface Sci.* **134** 198; 1989 *J. Colloid Interface Sci.* **127** 35, 48
[5] Zgrablich G, Mendioroz S, Daza L, Pajares J, Mayagoitia V, Rojas F and Conner W C 1991 *Langmuir* **7** 779
[6] Mayagoitia V, Rojas F and Kornhauser I 1985 *J. Chem. Soc., Faraday Trans.* I **81** 2931
[7] Mayagoitia V, Rojas F and Kornhauser I 1988 *J. Chem. Soc., Faraday Trans.* I **84** 785
[8] Mayagoitia V, Gilot B, Rojas F and Kornhauser I 1988 *J. Chem. Soc., Faraday Trans.* I **84** 801
[9] Essam J W 1972 *Phase Transition and Critical Phenoman* vol 2, ed C Domb and M S Green (New York: Academic)
[10] Coniglio A 1976 *Phys. Rev.* B **13** 2194
[11] Faccio R J, Zgrablich G and Mayagoitia V 1993 *J. Phys.: Condens. Matter* **5** 1823
[12] Vidales A M, Faccio R J, Riccardo J L, Miranda E N and Zgrablich G submitted
[13] Everett D H and Rojas F 1988 *J. Chem. Soc., Faraday Trans.* I **84** 1455
[14] Scholten J J F, Beers A M and Kiel A M 1975 *J. Catal.* **36** 23
[15] De Witt L A and Scholten J J F 1975 *J. Catal.* **36** 30
[16] Conner W C, Blanco C, Coyne K, Neil J, Mendioroz S and Pajares J 1988 *Characterization of Porous Solids* ed K K Unger *et al* (Amsterdam: Elsevier) p 273