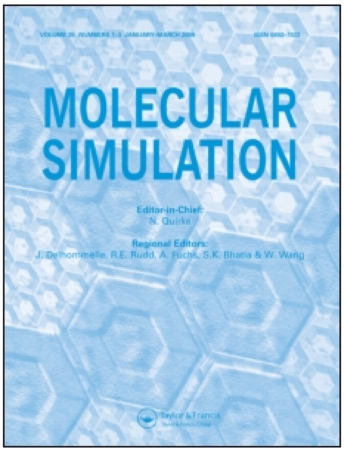

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Pitard, E. , Rosinberg, M. L. and Tarjus, G.(1996) 'Thermodynamics of Fluids in Disordered Porous Materials', Molecular Simulation, 17: 4, 399 — 419

To link to this Article: DOI: 10.1080/08927029608024118

URL: http://dx.doi.org/10.1080/08927029608024118

Molecular Simulation, 1996, Vol. 17, pp. 399–419
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THERMODYNAMICS OF FLUIDS IN DISORDERED POROUS MATERIALS

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(Received December 1995; accepted April 1996)

When a fluid is adsorbed in micro or meso-porous materials such as aerogels or porous glasses, its thermodynamic behavior is considerably altered. The changes result from the combined effect of geometric confinement, randomness of the matrix, and connectivity of the pore network, whose understanding requires a good theoretical description of the matrix microstructure and its interaction with the fluid particles. We present a liquid-state formalism in which the fluid-matrix system is modeled as a 'quenched-annealed' binary mixture formed by the matrix particles (quenched species) and the fluid particles (annealed species); the averaging over quenched disorder is handled via the replica method. Model calculations for the phase diagram of the confined fluid within the mean spherical approximation show that for sufficiently attractive matrix-fluid interaction, the liquid-gas transition has a higher critical density than that of the bulk fluid and is accompanied by an additional "pre-condensation" transition. In addition, the results obtained within various standard approximation schemes suggest that the behavior of the fluid at its liquid-gas critical point is the same as that of the random field Ising model (RFIM).

Keywords: Thermodynamics, porous materials; quenched-annealed systems

I. INTRODUCTION

The static as well as the dynamic properties of a single component fluid and a binary mixture are dramatically modified when they are imbibed in disordered micro or mesoporous materials. This has been known for many years, but interest has been revived by new data that have been recently obtained in a number of experiments on near critical fluids adsorbed in various porous materials like glasses [1] and dilute silica networks [2, 3]. If much progress has been made in the study of wetting effects and capillary condensation in model porous systems for which randomness associated with the distribution of pore sizes and shapes is negligible [4], the understanding of related phenomena in *disordered* media is still very partial. Among the issues that remain controversial is the very existence of phase transitions in such media. For instance, a common interpretation relies on a description of porous materials by means of a distribution of *independent* pores of various sizes. In such a model, the phase transitions that may occur in each pore are smeared out by averaging over the pore distribution, thereby preventing the appearance of a well-defined macroscopic phase transition [5].

On the experimental side, no definite conclusions have yet been reached. In the case of porous glasses such as Vycor, where the porosity is small (~30%) and the mean pore radius is about 30 Å, light scattering and small-angle neutron scattering experiments on near critical binary mixtures [1] show no macroscopic phase separation, but a "transition" to a frozen-domain state that is strongly history-dependent. At this transition, the shape of the structure factor appears to change from Lorentzian to a combination of Lorentzian and Lorentzian squared contributions with a correlation length that does not exceed the mean pore size. In addition, there is some indication that, as a function of temperature, some kind of complete to partial wetting "transition" occurs before the appearance of the frozen domain state. Single component fluids have also been studied in Vycor. In an experiment on N_2 using positronium annihilation spectroscopy [6], capillary condensation of the adsorbed gas to a dense liquid-like state filling the pores has been observed at a pressure which is less than the saturated vapor pressure in the bulk (see Fig. 1). This is quite similar to what has been predicted for a fluid in a slit-shaped or cylindrical pore, where there is a shift from the bulk condensation transition arising from finite-size effects [4]. On the other hand, the observed hysteresis could also be due to nonequilibrium network effects, such as a pore blocking mechanism [7].

Quite different porous materials are provided by silica aerogels. They are formed by very dilute disordered networks of silica strands that occupy only a few percent of the total volume (the porosity can be as high as 95 to 98 %). They also display a volume fractal character with no dominant length scale from 20 to 2000 Angströms. In such systems, confinement plays a marginal role and proper phase transitions have indeed been observed by heat capacity measurements and light scattering. Wong and Chan [3] have studied the liquid-gas phase transition of ^{4}He and N_2. Compared to the bulk case, the critical point is displaced to a lower temperature and a higher density whereas the width of the coexistence curve is dramatically reduced (by an

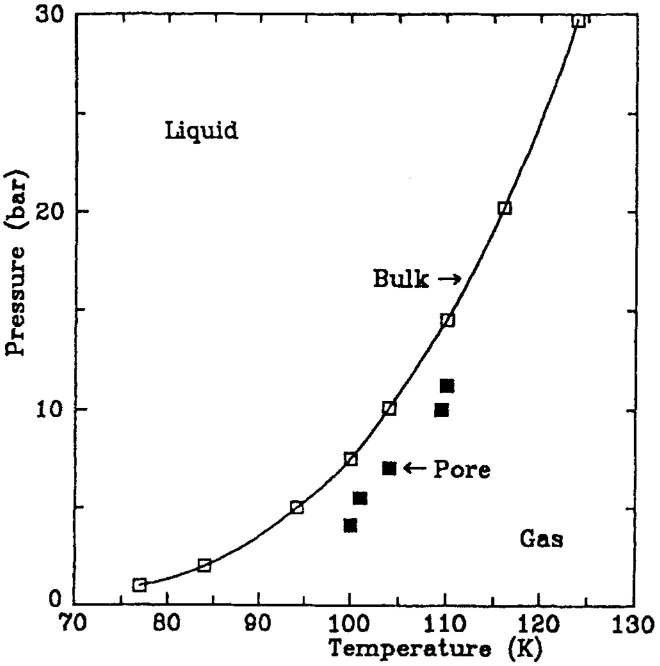

FIGURE 1 Partial phase diagram for N_2 in Vycor and bulk N_2 (from Wilkinson *et al.* [6]).

order of magnitude). The experimental data for ^{4}He are reproduced in Figure 2.

Theoretical interpretations are faced with the difficult task of taking into account the effects of confinement, randomness, and connectivity of the pore network, as well as wetting phenomena. We have already mentioned the description in terms of independent pores which includes confinement and some kind of randomness, but neglects the fact that the pores form a connected network. A quite different point of view has been taken by Brochard and de Gennes [8] who proposed that near critical binary mixtures (and by extension single component fluids) in a porous medium can be considered as experimental realizations of the random-field Ising model (RFIM). Confinement plays no role in their picture, and the model is more likely then to be applicable to silica aerogels. Their argument relies on two effects, preferential adsorption and randomness. If the silica strands prefer one phase over the other, an adsorbed layer is formed, resulting in a shift in the composition of the free fluid in the middle of the pores. This shift is random because the silica network is disordered and it can be described in

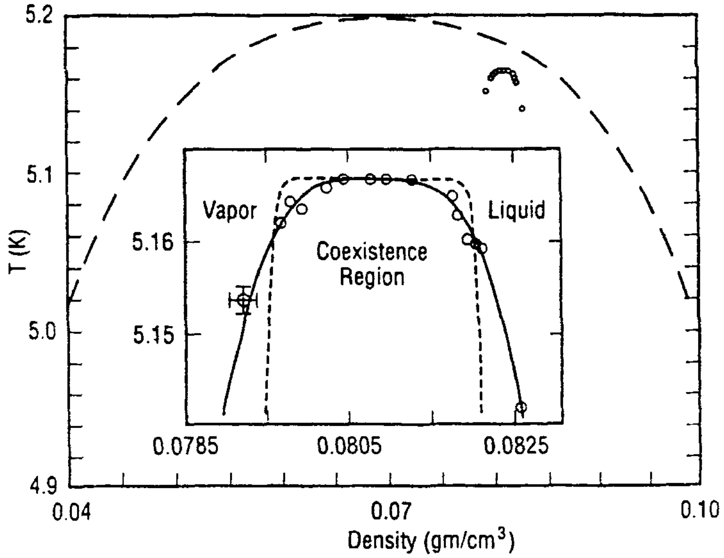

FIGURE 2 Liquid-vapor coexistence curve of ^{4}He in aerogel taken from A. P. Y. Wong and M. H. W. Chan [3]. The circles depict the locations of sharp heat-capacity peaks associated with the coexistence boundary. The broken line is the coexistence curve of pure ^{4}He. The inset magnifies the coexistence boundary in aerogel.

terms of a random contribution to the chemical potential, or, in an Ising spin representation, in terms of a random magnetic field. When close enough to the critical point, the correlation length of the fluid becomes much larger than the mean pore size, and one can coarse-grain the system. The behavior of the fluid is then related to that of the random-field Ising model whose Hamiltonian is given by

$$\mathscr{H} = -J\sum_{\langle ij\rangle} s_i s_j - \sum_i h_i s_i, \tag{1}$$

where $J > 0$ is an exchange coupling between spins s_i, s_j on nearest neighbor sites that induces a ferromagnetic transition in the absence of magnetic fields; the h_i's are local random fields that obey some given distribution. Usually, one assumes that there are no correlations among fields at different sites and one chooses a gaussian or a symmetric bimodal distribution for the single-site fields. This system has been extensively studied for the past twenty years [9]. Although its critical behavior is still not fully understood, it displays some of the features experimentally observed in porous media: the displacement of the critical point to lower temperatures, the appearance of a Lorentzian-squared contribution in the structure factor, the very slow, activated dynamics, and the nonexponential shape of the dynamic correlation functions. However, there are also several experimental features that are not compatible with the RFIM, like the observed critical exponent of the coexistence curve of ^{4}He and N_2 in silica aerogels or the displacement of the critical point to higher densities.

Alternative explanations that totally neglect the effect of randomness have also been proposed [10, 11]. Several experimental observations on binary mixtures in Vycor have for instance been interpreted in terms of wetting phenomena in a single pore under the constraint of fixed overall composition [10].

This brief survey suggests that further progress calls for an approach which, contrary to all previously described ones, embodies confinement, randomness, and connectivity of the pore network together. This implies a more reasonable description of the structure of the matrix and, in order to account for wetting effects, of its interaction with the fluid. Our goal is thus to generalize the techniques of liquid-state theory in order to study fluids confined in disordered materials. We present in this paper the first steps we have made in this direction.

II. STATISTICAL MECHANICS OF A QUENCHED-ANNEALED SYSTEM

When a fluid is imbibed in a random matrix that is statistically homogeneous on a macroscopic scale, it is submitted to a 3-dimensional external potential created by the matrix particles. The standard methods for treating fluids in external potentials, like density functional theory [12], can no longer be used because the potential varies irregularly throughout the sample and is therefore very complicated. Dividing the system into a large number of macroscopic subsamples or "realizations" having a different, but fixed, distribution of the matrix particles, one can consider the properties of the fluid in each subsample and then average over all possible realizations. Hopefully, the thermodynamics, for instance the free energy, and the structural quantities, like the fluid pair correlation functions or the fluid structure factor, will be "self-averaging", which means that their value for a macroscopic volume of the material coincides with their average over the various realizations. A major interest of the averaging process is that translational symmetry is then recovered in the statistical mechanical treatment.

Following the original ideas of Madden and Glandt [13], our approach starts thus with a description of the probability distribution for the matrix configurations. The simplest situation from a theoretical point of view is when the matrix is produced by a quench from some higher temperature T_0 at which the system was in thermal equilibrium. For a realization containing N_0 matrix particles located at $\{\mathbf{q}_1, \mathbf{q}_2 ... \mathbf{q}_{N_0}\}$, the probability distribution is then given by the Gibbs measure, $P_0(\mathbf{q}^{N_0}) = 1/Z_0 \exp[-\beta \mathscr{H}_{00}(\mathbf{q}^{N_0})]$, where $\mathscr{H}_{00}$ is the Hamiltonian of the matrix alone and $Z_0 = 1/N_0! \int \mathbf{dq}^{N_0} \exp[-\beta \mathscr{H}_{00}(\mathbf{q}^{N_0})]$ is the partition function. Of course, one must assume that no major structural relaxation took place during the quench. For instance, in the case of porous glasses, describing the matrix structure by quenched equilibrium configurations of a hard sphere fluid or by randomly distributed penetrable spheres provides a reasonable approximation. In this case, the temperature T_0 is irrelevant and can be as well replaced in $P_0(\mathbf{q}^{N_0})$ by the temperature at which the real experiment is performed. Such a description is certainly not valid for an aerogel. The configurations then can be more realistically obtained by an off-equilibrium cluster-cluster aggregation process [14]. Our formalism can be extended to describe such cases, but for the sake of simplicity, we restrict ourselves now on to the consideration of quenched equilibrium configurations.

Let introduce into the matrix the fluid particles, which are denoted by the index 1, and let them equilibrate at some temperature T with a reservoir fixing the chemical potential μ_1. This corresponds to the experimental situation when one performs gas adsorption isotherms measurements. The system under study is therefore a *binary* mixture in which some particles, the matrix particles 0, are quenched and the others, the fluid particles 1, are "annealed". This is represented in Figure 3. We now want to obtain the thermodynamic and structural quantities of this quenched-annealed (Q-A) mixture. We first consider the average fluid grand potential $\bar{\Omega}_1$, which is the logarithm of the matrix-dependent grand partition function $\Xi_1(\mathbf{q}^{N_0})$, averaged over the realizations of the matrix,

$$-\beta \bar{\Omega}_1 = \frac{1}{Z_0 N_0!} \int d\mathbf{q}^{N_0} \exp[-\beta H_{00}(\mathbf{q}^{N_0})] \ln \Xi_1(\mathbf{q}^{N_0}) \tag{2}$$

Two methods have been proposed for studying $\bar{\Omega}_1$. The first one, developed by Madden and Glandt [13], consists in using the standard graph theoretical techniques of topological reduction, carefully analyzing the constraints on the cluster expansions induced by the fact that the matrix particles are fixed. The second one, which is more powerful, consists in using

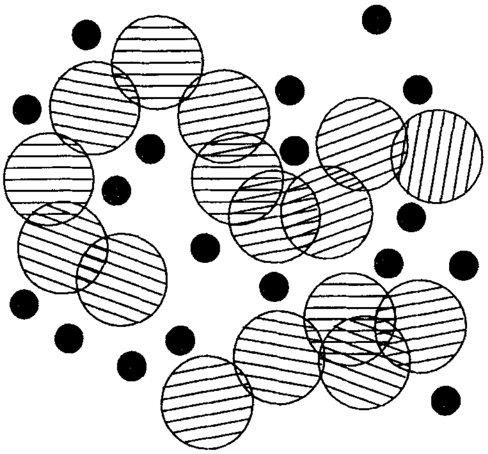

FIGURE 3 Schematic view of a quenched-annealed mixture. Matrix and fluid particles are represented by large and small disks, respectively.

the replica method. This is a standard method for studying disordered systems, such as spin glasses, and it has been extended to continuum fluids in refs. [15–17] (for an earlier use of the replica method in the context of the theory of liquids, see ref. [18]).

The starting point is the identity $\ln \mathbf{X} = \lim_{s \to o} d\mathbf{X}^s/ds$ from which we get immediately that $\bar{\Omega}_1$ is $1/Z_0$ times the limit when s goes to zero of the derivative of the grand potential of an equilibrium mixture with $(s+1)$ components: s fluid replicas plus the matrix particles, which are now considered as annealed. The s fluid replicas do not interact between each other but they interact with the matrix. *Therefore, we have replaced the original Q–A binary mixture by a multicomponent equilibrium mixture for which we can use the standard methods of liquid-state theory.* We can formally write cluster expansions, integral equations, thermodynamic relations for this $(s+1)$ mixture, and at the end take the limit $s \to 0$, assuming that there is no problem in performing the analytic continuation for noninteger values of s. There might be some circumstances in which the procedure is not valid and the analytic continuation must be carried out by allowing for a breaking of the permutation symmetry between replicas [19] (note that in such cases, the cluster expansion method breaks down as well). This problem will be addressed in future work, and, in what follows, we assume that the $s \to 0$ limit can be safely taken and that all replicas are equivalent. Then, one can derive a set of Ornstein-Zernike equations, which can be called the Replica Symmetric Ornstein-Zernike (RSOZ) equations, relating the total pair correlation functions of the quenched-annealed mixture to the corresponding direct correlation functions [16],

$$h_{00}=c_{00}+\rho_0 c_{00}\otimes h_{00} \tag{3}$$

$$h_{10}=c_{10}+\rho_0 c_{10}\otimes h_{00}+\rho_1 c_c\otimes h_{10} \tag{4}$$

$$h_{11}=c_{11}+\rho_0 c_{10}\otimes h_{01}+\rho_1 c_c\otimes h_{11}+\rho_1 c_b\otimes h_c \tag{5}$$

$$h_c=c_c+\rho_1 c_c\otimes h_c \tag{6}$$

where the symbol $\otimes$ denotes a convolution, $h_{01}=h_{10}$ and $c_{01}=c_{10}$ by symmetry, and ρ_i is the average density of species i. As usual, the c's are the non-nodal part of the h's. Note that the equation for the matrix decouples from the other ones because the matrix configurations do not depend on the fluid. The fluid-fluid correlation function $h_{11}(r)$ is defined as usual from the average fluid-fluid pair density, $h_{11}(r)=\rho_{11}^{(2)}(r)/\rho_1^2-1$; however, because of the correlations between fluid particles induced by the quenched matrix, h_{11} must be split into a connected part h_c and a disconnected or blocking part h_b that are defined in the following way [17]:

$$\rho_1^2 h_c(r_{12})=\rho_{11}^{(2)}(r_{12})-\overline{\rho_1(\mathbf{r}_1;\mathbf{q}^{N_0})\,\rho_1(\mathbf{r}_2;\mathbf{q}^{N_0})} \tag{7}$$

and

$$\rho_1^2 h_b(r_{12})=\overline{\rho_1(\mathbf{r}_1;\mathbf{q}^{N_0})\,\rho_1(\mathbf{r}_2;\mathbf{q}^{N_0})}-\rho_1^2 \tag{8}$$

where the overbar represents an average over matrix configurations. Similarly, $c_{11}(r)$ is decomposed into its connected and blocking contributions, c_c and c_b. An important feature is that h_c and h_b have a different behavior near the critical point, h_b, and therefore h_{11}, being much longer ranged than h_c [20].

Now, assuming that some closure relations are chosen to solve the RSOZ equations, so that the correlation functions are known, how can one compute the thermodynamics? Usually, there are several routes available. The first one is the compressibility equation which, for the Q-A mixture, relates the derivative of the fluid pressure with respect to the density, χ_1, to the value of the Fourier transform $\hat{h}_c$ at $k=0$ [17,21]:

$$k_B T\rho_1\chi_1 = 1+\rho_1\hat{h}_c(0) \qquad (9)$$

What we call the pressure here is the derivative of the fluid grand potential with respect to the total volume of the sample at constant temperature, fluid chemical potential and density of the matrix. This is the thermodynamic potential conjugated to the volume. We have shown [17] that it satisfies the Gibbs-Duhem relation $dP_1=\rho_1\ d\mu_1|_{T,\rho_0}$, so that it can in principle be obtained by integration of an experimental adsorption isotherm. We insist on this point since there has been some discussion in the litterature about the microscopic definition of the pressure [22]. In particular, this thermodynamic pressure, which should be better called the grand potential density, does not identify to the mechanical pressure that is obtained by averaging the stress tensor over quenched disorder [23]. Therefore, contrary to the case of bulk fluids, the condition of mechanical equilibrium does not reveal any useful information about the thermodynamics of fluids in disordered porous media. For related reasons, the virial route to the pressure is hardly praticable. For Q-A mixtures, it can be derived by using either the replica trick [17] or the Green-Bogoliubov dimensional rescaling argument in the grand canonical ensemble for the matrix [23]. However, the resulting expression contains terms that cannot be calculated from the pair correlation functions.

An alternative route is via the energy. The expression of the internal energy is simply

$$U_1/V=\int d\mathbf{r}\,\{1/2\rho_1^2 v_{11}(r)\,[1+h_{11}(r)]+\rho_0\rho_1 v_{01}(r)\,[1+h_{01}(r)]\} \qquad (10)$$

where $v_{11}(r)$ and $v_{10}(r)$ are the fluid-fluid and fluid-matrix interaction potentials, respectively. From this equation, one can obtain the fluid Helmholtz free energy by integrating with respect to temperature.

Finally, very recently, Glandt and coworkers [24] have suggested to use the scaled particle theory to compute the thermodynamic properties for hard sphere particles. It is essentially a "charging" process where the diameters of the particles are increased from zero to their real values. This is therefore a rather demanding procedure from a computational point of view.

III. MEAN-FIELD APPROXIMATION

For purely repulsive systems such as hard sphere fluids inside a hard sphere matrix or a random sphere matrix, it has been found that standard closure relations to the RSOZ equations like the Percus-Yevick or the hypernetted-chain equation yield predictions for the pair correlation functions in good agreement with Monte-Carlo simulations [25]. The case where attractive interactions are present both between the matrix and the fluid particles and between the fluid particles themselves is more interesting but has been little studied so far [26]. The simplest theory that one can build is a van der Waals-like mean-field theory [27, 28]. Assuming that each of the pair potentials $v_{11}(r)$ and $v_{10}(r)$ can be split into a reference (repulsive) part and a perturbative (attractive) part, $w_{11}(r)$ and $w_{10}(r)$, and neglecting correlations between particles when calculating the contribution of the perturbative part to the Helmholtz free energy of the fluid in the matrix, one gets

$$\bar{F}_1/V = \bar{F}_1^0/V + \rho_1^2/2 \int d\mathbf{r} w_{11}(r) + \rho_o \rho_1 \int d\mathbf{r} w_{01}(r), \tag{11}$$

where $\bar{F}_1^0$ is the free energy of the reference system. Since this equation has the van der Waals form, it is able to predict the occurence of a vapor-liquid equilibrium ("capillary" condensation) in the system. Coexistence envelopes are shown in Figure 4 in the case of a square-well fluid inside a hard sphere matrix [27]. Each curve corresponds to a different value of the matrix density. One can see a decrease of the critical temperature and of the critical density from their bulk values, the latter feature being at variance with experimental observations [3]. Moreover, there is no significant shrinking of the coexistence curve width. But the principal weakness of Eq. (11) is that it neglects the competition between fluid-fluid and fluid-matrix attractive interactions: varying the relative strength of these interactions does not alter the shape of the phase diagram. Clearly, one needs a more sophisticated treatment of microscopic correlations.

IV. MEAN-SPHERICAL APPROXIMATION FOR A LATTICE GAS MODEL

In order to perform a detailed investigation of the phase diagram, we shall now consider a lattice gas version of a fluid in a disordered matrix [20].

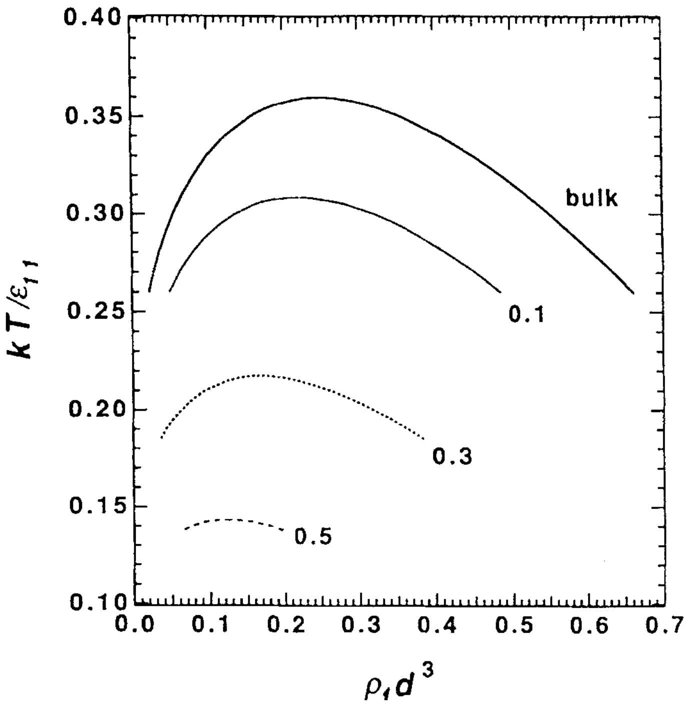

FIGURE 4 Coexistence envelopes for a square-well fluid inside a hard sphere matrix calculated in the mean-field approximation (from D. M. Ford and E. D. Glandt [21]). ε_{11} and d are the well depth and the hard core diameter, respectively. The curves are labeled by the values of the reduced matrix density $\rho_0 d^3$.

Lattice gas models of confined fluids have been extensively studied by simulation or theory in recent years [29], and it has been shown that despite the very poor treatment of short-range correlations, phase transitions and adsorption phenomena found in these systems have their direct counterparts in the continuum case. Therefore, we expect that the phase diagram of our model will incorporate the essential physical features of that of a real system. In addition, it will be easier to make contact with the conceptual framework of the random-field Ising model.

A. Theory

We consider nearest-neighbor (n.n.) interactions on a d-dimensional hypercubic lattice. Lattice cells (or sites) can be occupied either by matrix or fluid "particles" and the pair potentials contain a "hard-core" part which excludes multiple occupancy of a cell (or site).

The Hamiltonian is

$$\mathcal{H} = -w_{11}\sum_{\langle ij\rangle}\tau_i\tau_j\eta_i\eta_j - w_{01}\sum_{\langle ij\rangle}[\tau_i\eta_i(1-\eta_j)+\tau_j\eta_j(1-\eta_i)], \tag{12}$$

where τ_i is the fluid occupancy variable at site i ($\tau_i=0$ or 1) and η_i are (quenched) site disorder variables taking the values 0,1 at random and such that $\overline{\eta_i} = 1-\rho_0$; $w_{11}>0$ and w_{01} are the fluid-fluid and fluid-matrix n.n. interactions and the sums are over n.n. pairs of sites. Therefore, in this model, the matrix is only characterized by its density ρ_0 and by the interaction ratio $y=w_{01}/w_{11}$. The fluid particles are in equilibrium with an external reservoir which fixes their chemical potential μ_1 and thus, at a given temperature, the average fluid density in the matrix is $\rho_1=\overline{\langle\tau_i\rangle}$, where $\langle\cdot\rangle$ denotes the thermal average. It must be noted that there is no hole-particle symmetry for the fluid because of the interaction with the matrix. More precisely, one has the general symmetry property

$$\rho_1(\mu_1,T,y,\rho_0)+\rho_1(-\mu_1-w_{11}c,T,1-y,\rho_0)=1-\rho_0 \tag{13}$$

where c is the coordination number of the lattice. The usual equivalence between the lattice gas and the spin 1/2 model shows that we are actually dealing with a site diluted Ising model with asymmetric correlated random fields [30]. Therefore, there is no exact correspondence between this microscopic description of a fluid inside a matrix and the usual RFIM. The special case $y=1/2$ is equivalent to the site diluted Ising model [31] and a limited numerical study by Monte Carlo simulations was performed for $y=1$ some years ago [32].

We use the mean-spherical approximation (MSA) in replica space to close the OZ equations for the $s+1$-species equilibrium mixture (see section II). In the $s\to0$ limit, this yields

$$c_b(\mathbf{r})=0$$

$$c_c(\mathbf{r})=c_c^0\delta_{\mathbf{r},0}-\beta w_{11}(\mathbf{r})$$

$$c_{01}(\mathbf{r})=c_{01}^0\delta_{\mathbf{r},0}-\beta w_{01}(\mathbf{r}) \tag{14}$$

where c^0_{01} and c^0_c are functions of temperature and fluid density, that, owing to the structure of the RSOZ equations, Eqs. (3–6), are completely determined by imposing the core conditions $h_{01}(\mathbf{r}=0) = h_{11}(\mathbf{r}=0) = -1$. Note that h_c and h_b do not satisfy themselves the core requirement. On the other hand, the core condition for the matrix particles $h_{00}(\mathbf{r}=0) = -1$ readily yields $c_{00}(\mathbf{r}) = -\delta_{\mathbf{r},0}/(1-\rho_0)$.

Generalizing the analysis developed by Stell [33] and Theumann [34] for the bulk lattice gas, one can solve the RSOZ equations analytically in terms of the lattice Green's function $P(\mathbf{r},z)$ defined, for instance for a d-dimensional b.c.c. lattice ($c=2^d$), as

$$P(\mathbf{r},z)=\frac{1}{(2\pi)^d}\int_{-\pi}^{\pi} d^d\mathbf{k}\frac{e^{i\mathbf{k}.\mathbf{r}}}{1-z\Pi_{j=1}^d \cos k_j} \tag{15}$$

where $\mathbf{k}=(k_1,\ldots,k_d)$ and $0\leqslant z\leqslant 1$. After some calculations, one finds

$$\rho_1[\delta_{\mathbf{r},0}+\rho_1 h_c(\mathbf{r})]=\frac{T}{c}zP(\mathbf{r},z) \tag{16}$$

$$\rho_1^2 h_b(\mathbf{r}) = \rho_0(1-\rho_0)\left[(\Delta y+\tfrac{1}{2})^2\delta_{\mathbf{r},0}-2(\Delta y+\tfrac{1}{2})(\Delta y-\Delta r)\frac{P(\mathbf{r},z)}{P(z)}\right.$$
$$\left.+(\Delta y-\Delta r)^2\frac{zP'(\mathbf{r},z)+P(\mathbf{r},z)}{P(z)^2}\right] \tag{17}$$

$$\rho_1 h_{01}(\mathbf{r})=(1-\rho_0)\left[-(\Delta y+\tfrac{1}{2})\delta_{\mathbf{r},0}+(\Delta y-\Delta r)\frac{P(\mathbf{r},z)}{P(z)}\right] \tag{18}$$

where $\Delta r=\rho_1/(1-\rho_0)-1/2, \Delta y=y-1/2, P(z)=P(\mathbf{0},z)$ and $P'(\mathbf{r},z)=\partial P(\mathbf{r}, z)/\partial z$. T is the temperature given in units of w_{11}/k_B and z is solution of the equation

$$\frac{T}{c(1-\rho_0)}=\frac{1}{zP(z)}\left[\frac{1}{4}-\Delta r^2-\rho_0(\Delta y-\Delta r)^2 z^2\frac{d}{dz}\left(\frac{1}{z}-\frac{1}{zP(z)}\right)\right] \tag{19}$$

For the b.c.c. lattice, $P(z)$ identifies to the generalized hypergeometric function ${}_dF_{d-1}(\{1/2\},\{1\}|z^2)$ [35].

In order to obtain the phase diagram of the lattice fluid, we calculate the Helmholtz free energy via the energy route (see above). The MSA-energy route generally gives a good description of the thermodynamic properties of model homogeneous fluids. For the lattice gas system under study, it is identical to the well known optimized random phase approximation [36]. Convenient expressions in terms of the direct correlation functions in Fourier space have been worked out by Hoye and Stell [37] in the case of fluid mixtures. Using these expressions for the $s+1$-species equilibrium mixture in replica space and then taking the $s \to 0$ limit gives analytical expressions for the fluid free energy, the thermodynamic pressure P_1 and the chemical potential μ_1. For instance, one finds

$$-\frac{\mu_1}{T} = \ln\left[\frac{\frac{1}{2}-\Delta r}{\frac{1}{2}+\Delta r}\right] + \frac{1}{2(1-\rho_0)}\left[\frac{1}{\frac{1}{2}-\Delta r} - \frac{1}{\frac{1}{2}+\Delta r}\right]$$

$$+\frac{c}{T}\left[\frac{1}{2} - \Delta r\left(\frac{1}{z}-1\right) - \rho_0(\Delta y - \Delta r)\left(\frac{1}{z} - \frac{1}{zP(z)} - 1\right)\right] \quad (20)$$

where μ_1 is given in w_{11} units. Therefore, for given values of ρ_0 and y, one first solves Eq. (19) to get z as a function of T and ρ_1, and then replaces z in Eq. (20) to get the chemical potential. Equality of the chemical potentials inside and outside the matrix (obtained by setting $\rho_0 = 0$ in Eqs. (19) and (20)) yields adsorption isotherms.

B. Phase Diagram and Critical Behavior

The phase diagram of the lattice fluid inside the matrix is obtained as usual by solving the system

$$\begin{aligned} P_1(\rho_{1g}) &= P_1(\rho_{1l}) \\ \mu_1(\rho_{1g}) &= \mu_1(\rho_{1l}) \end{aligned} \quad (21)$$

We have shown elsewhere [20] that the thermodynamic inconsistency of the MSA has more severe consequences for systems with quenched disorder than for systems without disorder because of the stronger divergence of the blocking part $h_b(r)$ of the pair correlation function at the critical point. In particular, the compressibility route yields no phase transition for $d \leqslant 4$. In view of this difficulty, we first consider the case of a 5-dimensional lattice. The effect of the matrix-fluid interaction on the shape of the coexistence envelope at a fixed value of the matrix density is shown in Figure 5. For

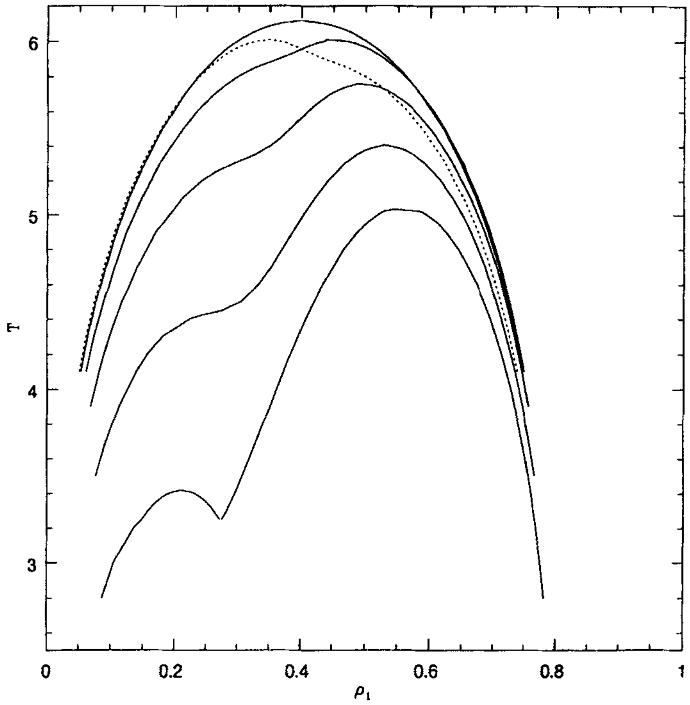

FIGURE 5 Coexistence envelopes for the matrix-fluid lattice gas model caculated via the MSA-energy route. $d = 5$ and $\rho_0 = 0.2$. From top to bottom, the solid lines correspond to $y = 0.5$, 1, 1.5, 2, and 2.4; the dotted line corresponds to $y = 0$.

$y = 0$, which means that there is no matrix-fluid interaction apart from the hard-core part which excludes fluid particles from occupying a fraction ρ_0 of sites, the gas-liquid critical density is less than the bulk value 1/2. As y increases, we observe a decrease of the critical temperature associated to the gas-liquid transition (capillary condensation) and an *increase* of the critical density that becomes larger than 1/2 for $y \simeq 1.5$; this displacement of the critical point from the bulk value is now in agreement with experiments. There is also a significant shrinking of the coexistence envelope. When y is too large, the gas-liquid transition disappears. This is observed as well for large enough ρ_0 at a fixed value of y.

The most striking feature in Figure 5 is the appearance of a shoulder on the gas side for $y \simeq 1$, which eventually becomes a true second transition. This "pre-condensation" transition may correspond to a bridging of liquid domains appearing in the regions where the matrix sites are locally more

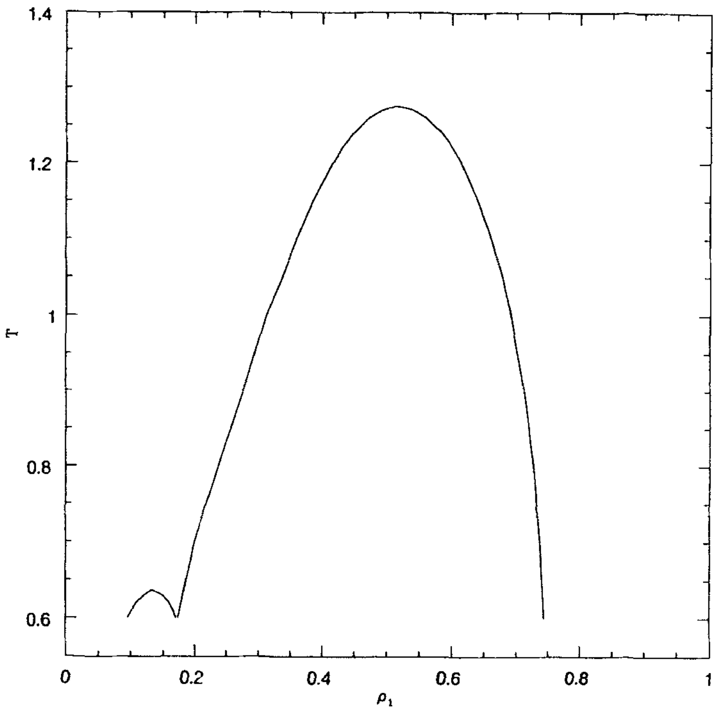

FIGURE 6 Coexistence envelope for the matrix-fluid lattic gas model calculated via the MSA-energy route ($d = 3$, $\rho_0 = 0.25$, $y = 1$).

dense. We have also found it in 3-*d*, as shown in Figure 6[1]. Note that the narrowing of the liquid-gas coexistence envelope is too small compared to experimental data (see Fig. 2); this quantitative discrepancy is expected in view of the too crude description of the microstructure of the porous material that is embodied in the present lattice gas model. The 3-d "adsorption" isotherms (fluid density inside the matrix vs chemical potential) at three different temperatures are shown in Figure 7. For a given value of ρ_0, the second transition only exists when $y(or\ \Delta y = y - 1/2)$ lies in a very small interval represented as a shaded region in Figure 8. This might explain why the transition has not be observed experimentally. We recall that, because of the symmetry property (13) which is fulfilled by the MSA

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[1] Very recently, this second transition has been observed in Monte Carlo simulations for a continuum model representing the adsorption of Lennard-Jones molecules in silica gel (K. S. Page and P. A. Monson, private communication).

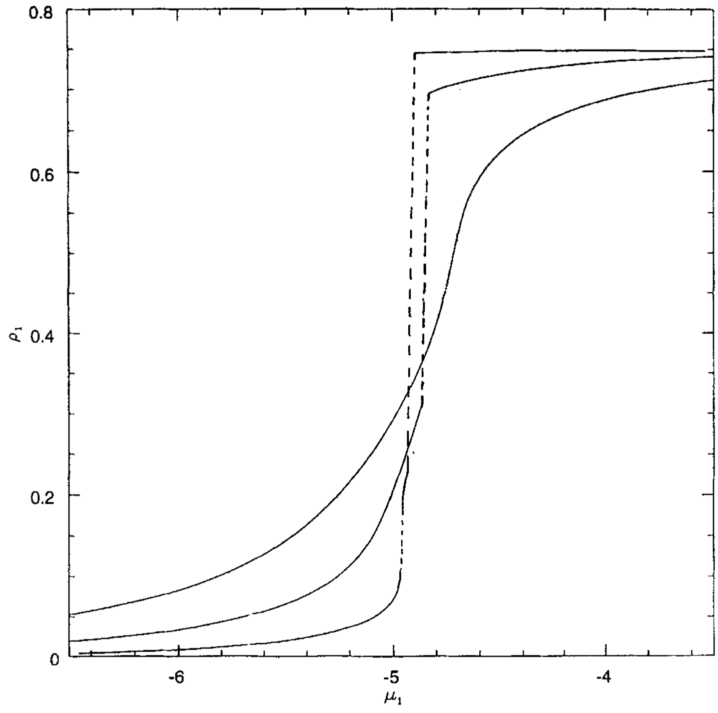

FIGURE 7 Adsorption isotherms ρ_1 vs μ_1 for the matrix-fluid lattic gas model calculated via the MSA-energy route ($d = 3$, $\rho_0 = 0.25$, $y = 1$). Three temperatures are displayed: from top to bottom on the left side of the graph, $T = 1.4$, 1, 0.62. The vertical parts of the isotherms corresponding to first order transitions are shown in dashed lines. Note for the $T = 0.62$ isotherm the occurrence of two discontinuous jumps.

solution, one has only to consider the case $y > 1/2$: if the matrix-fluid interaction w_{01} were sufficiently repulsive, one would have likewise a "pre-evaporation" transition associated with capillary evaporation. This behavior contrasts with that of the RFIM which exhibits only one phase transition.

Since the MSA is thermodynamically inconsistent, the critical behavior of the fluid inside the matrix depends on the route which is chosen to compute the free energy. By construction, the above energy route leads to classical (mean-field) exponents. On the other hand, for $d > 4$, the compressibility equation yields critical exponents for the gas-liquid transition which are identical to those of the spherical model of spins in a random field [20]. This suggests that the gas-liquid critical behavior is indeed related to that of the RFIM, as suggested by Brochard and de Gennes [8]. This is sup-

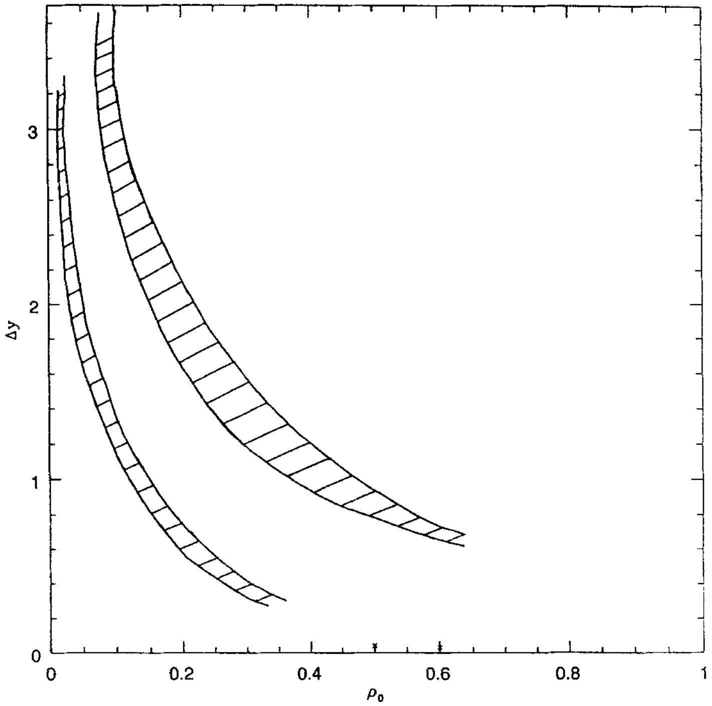

FIGURE 8 Domain of existence of the pre-condensation transition in the (Δy, ρ_0)-parameter space for $d = 3$ (lower shaded region) and $d = 5$ (upper shaded region). Only the $\Delta y \geqslant 0$ region is plotted; the $\Delta y \leqslant 0$ region is obtained by symmetry (see text).

ported by a preliminary study [30] in the framework of the so-called hierarchical reference theory of liquids which uses momentum-space renormalization group techniques [38].

V. CONCLUSION

In this paper, we have presented a liquid-state formalism applicable to fluids in disordered porous media. Our study of a lattice gas model in the mean spherical appoximation shows a rich phase behavior. The predicted gas-liquid transition exhibits features that are in qualitative agreement with experimental data in aerogels. This transition disappears when the matrix density is too large, which may correspond to experiments in Vycor. We have also found an additional "pre-condensation" transition for a rather narrow range of the matrix/fluid parameters. To confirm these results, we are now studying the MSA for continuum models that include a more realistic description of the matrix structure.

Acknowledgments

We are grateful to E. Kierlik, A. J. Liu, P. A. Monson and G. Stell for useful discussions.

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