# Capillary Condensation in Disordered Porous Materials: Hysteresis versus Equilibrium Behavior

E. Kierlik,[1] P. A. Monson,[2] M. L. Rosinberg,[1] L. Sarkisov,[2] and G. Tarjus[1]

[1]*Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France*
[2]*Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003*

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We study the interplay between hysteresis and equilibrium behavior in capillary condensation of fluids in mesoporous disordered materials via a mean-field density functional theory of a disordered lattice-gas model. The approach reproduces all major features observed experimentally. We show that the simple van der Waals picture of metastability fails due to the appearance of a complex free-energy landscape with a large number of metastable states. In particular, hysteresis can occur both with and without an underlying equilibrium transition, and thermodynamic consistency is not satisfied along the hysteresis loop.

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Capillary condensation of a gas inside a mesoporous material refers to the rapid change to a liquidlike state that occurs at a pressure (or chemical potential) lower than the bulk saturation value [1,2]. This phenomenon is often thought of as a shifted gas-liquid transition. Theoretical studies of fluids confined in single pores of ideal geometry have clarified the mechanism for such a shifted transition and introduced the concept of capillary criticality that describes the fact that the liquid-vapor critical point in a pore occurs at a lower temperature than in the bulk [2,3]. However, the situation in real mesoporous materials, such as porous glasses and silica gels, that consist of an interconnected network of pores of varying shape, curvature, and size is not as clear. With the possible exception of fluids in aerogels of very high porosity (95%–98%) for which a bona fide liquid-gas phase transition has been reported with no sign of hysteresis [4], there is no direct evidence of a first-order phase transition characterized, say, by a jump in the adsorbed amount of fluid, nor of true criticality signaled by density fluctuations on very large length scales. The typical experimental observation is the presence of a hysteresis loop in the sorption isotherms, a loop that is reproducible and vanishes at a temperature lower than the critical temperature of the bulk fluid [1,2,5]. The main questions raised by this phenomenology are: Is there a true phase transition associated with capillary condensation in disordered materials? What is the connection between this transition and the observed hysteresis? What are the sources of hysteretic behavior? No satisfactory answers have been provided so far.

In this Letter, we present a mean-field density functional theory of a disordered lattice-gas model. This model, introduced in a previous paper [6], incorporates the main physical ingredients characterizing fluids in disordered mesoporous media: preferential adsorption of one phase of the fluid, connectivity of the pore space, geometric and energetic disorder, exclusion effect due to the matrix. The present approach allows us to study for the first time the interplay between out-of-equilibrium (hysteresis) and equilibrium behavior associated with capillary condensation in a disordered matrix. We show that the theory captures the main aspects of the phenomenology of capillary condensation in real systems. The combination of disorder and interconnectivity of the pore network drastically alters the picture of capillary condensation built upon the independent-pore model [1,2,7] or the simple van der Waals description of metastability because it generates a complex free-energy landscape characterized by a large number of metastable states. In particular, we show that (i) hysteresis can occur *with* or *without* an underlying equilibrium phase transition, (ii) the disappearance of the hysteresis loop is not associated with capillary criticality, and (iii) thermodynamic consistency is not satisfied along the hysteresis loop.

The model is described by the following Hamiltonian:

$$\mathcal{H} = -w_{\mathrm{ff}} \sum_{\langle ij \rangle} \tau_i \eta_i \tau_j \eta_j - w_{\mathrm{mf}} \sum_{\langle ij \rangle} [\tau_i \eta_i (1 - \eta_j) + \tau_j \eta_j (1 - \eta_i)], \quad (1)$$

where $\tau_i = 0, 1$ and $(1 - \eta_i) = 0, 1$ denote the fluid and matrix occupancy variables, respectively, and the sums run over distinct pairs of nearest-neighbor (n.n.) sites. Although different disordered microstructures of the matrix may be considered [8], we choose here the simplest nontrivial case, a random matrix. The model is thus specified by two parameters, the average matrix density $\rho_m$ that fixes the porosity (equal to $1 - \rho_m$) and the ratio of the matrix-fluid over the fluid-fluid interactions, $y = w_{\mathrm{mf}}/w_{\mathrm{ff}}$, that determines the "wettability." In the following we consider only attractive matrix-fluid interactions [9] and we set $\rho_m = 0.25$. Most of the results are illustrated for a bcc lattice with linear size $L = 48$. When necessary, e.g., to check the existence of phase transitions, we have performed a finite-size analysis after averaging over several hundreds of matrix configurations.

The mean-field density functional theory (or equivalently for a lattice, the local mean-field theory) starts with the formulation of a free-energy functional of the fluid density field for a given matrix realization $\{\eta_i\}$:

$$\begin{aligned} F(\{\rho_i\}) = {} & \frac{1}{\beta}\sum_i [\rho_i \ln\rho_i + (\eta_i - \rho_i)\ln(\eta_i - \rho_i)] \\ & - w_{\mathrm{ff}} \sum_{\langle ij \rangle} \rho_i \rho_j \\ & - w_{\mathrm{mf}} \sum_{\langle ij \rangle} [\rho_i(1 - \eta_j) + \rho_j(1 - \eta_i)], \quad (2) \end{aligned}$$

where $\beta = 1/(k_B T)$ and $\rho_i = \langle \eta_i \tau_i \rangle$ is the average fluid density at site $i$. (The overall fluid density is then $\rho_f = (1/N)\sum_i \rho_i$, where $N = 2L^3$ is the total number of sites.) For a given chemical potential $\mu$, minimization of $\Omega(\{\rho_i\}) = F(\{\rho_i\}) - \mu \sum_i \rho_i$ with respect to the $\rho_i$'s provides the grand potential $\Omega$ of the adsorbed fluid. The corresponding equations for the fluid density on each site are

$$\rho_i = \frac{\eta_i}{1 + \exp\{-\beta[\mu + \sum_{j/i}(w_{\mathrm{ff}}\rho_j + w_{\mathrm{mf}}(1 - \eta_j))]\}}, \quad (3)$$

where the sum is over all n.n. of site $i$.

The above set of nonlinear coupled equations has been solved by means of a simple iteration algorithm according to two different protocols: (1) to mimic the experimental procedure, we follow continuously the solutions under small variations of the chemical potential $\mu$ (typically, $\Delta\mu/w_{\mathrm{ff}} = 10^{-3}$) and (2) to search more exhaustively the solution of Eq. (3) for a given $\mu$, we repeat the iteration procedure with a large number of initial conditions (typically, $10^2$) corresponding to uniform fillings of the lattice at different overall fluid densities (i.e., $\rho_i^{(0)} = \rho^{(0)}$).

We show in Fig. 1 typical isotherms obtained by increasing continuously $\mu$ from $-\infty$ (adsorption branch) and decreasing continuously $\mu$ from $+\infty$ (desorption branch). They look qualitatively similar to the experimental isotherms of fluids adsorbed in porous glasses and silica gels [1,2,5], with an asymmetric hysteresis loop characterized by a steep desorption branch and a smoothly increasing adsorption branch [9].

An important test for the relevance of any model of capillary condensation in disordered porous materials is the shape of the so-called "scanning curves," i.e., curves that are obtained by reversing the sign of the evolution of $\mu$ at different points along the adsorption or the desorption branches [7]. It has been stressed that these curves are not properly reproduced by the widely used independent-pore model [1,2,7]. An illustration of the scanning curves on adsorption and desorption obtained within the present theory is shown in Fig. 2. They look strikingly similar to those observed experimentally, with an upward curvature on adsorption and a downward curvature on desorption. When varying the chemical potential up and down along different paths we find a hierarchy of inner scanning curves, in close analogy to the hysteretic behavior displayed by a variety of systems [10–12]. Note that in contrast with network percolation models [12], we do not presuppose any rules for the evolution of the fluid configurations in the pore space and we need not introduce a specific description of the geometry at the junctions between pores.

The above results confirm that the present approach reproduces qualitatively the phenomenology associated with capillary condensation in porous glasses and silica gels.

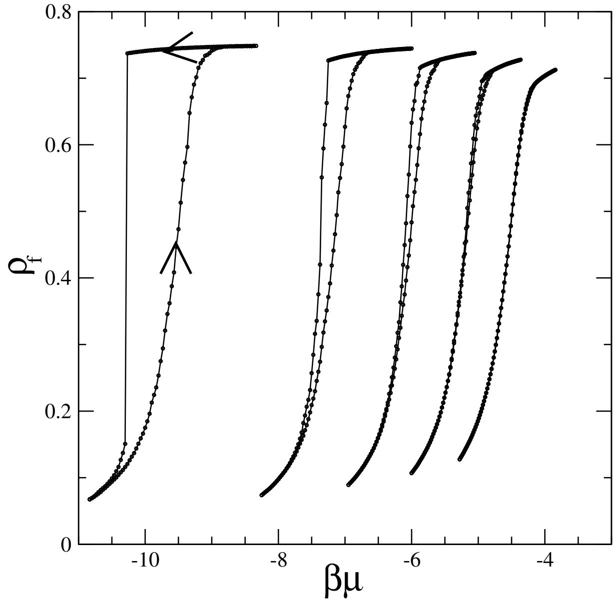

FIG. 1. Theoretical sorption isotherms for $y = 1.5$ at $T^* = k_B T/w_{\mathrm{ff}} = 0.6, 0.8, 0.95, 1.1$, and 1.25 (from left to right). The mean-field bulk critical point is at $T^* = 2$.

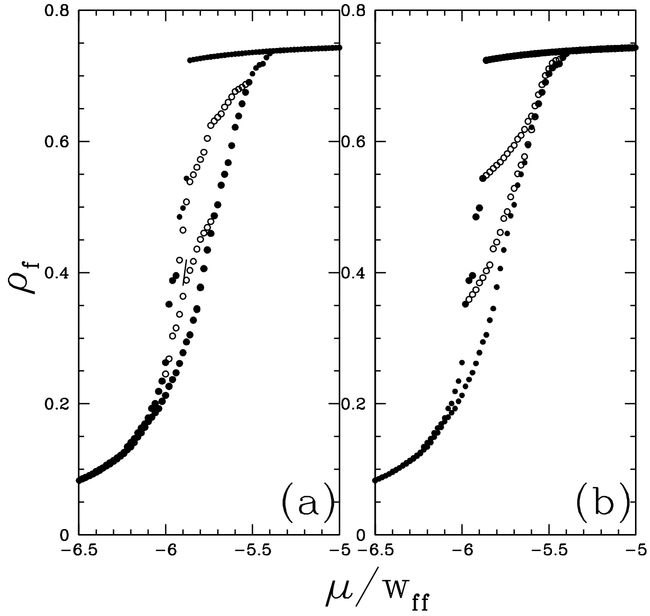

FIG. 2. Theoretical desorption (a) and adsorption (b) scanning curves (open circles) for $y = 1.5$ and $T^* = 0.8$.

This indicates that, despite its simplicity, our model Hamiltonian does capture the main physical features of fluids adsorbed in real mesoporous systems and that equilibration via thermally activated processes, processes that are absent in the mean-field description, does not substantially modify the picture. Indeed, the implicit assumption behind the direct comparison of the theoretical sorption curves with the experimental ones is that the system does not have time to equilibrate at constant $T$ and $\mu$ and that adsorption/desorption only proceeds under the influence of chemical-potential changes. (This assumption may break down when the perturbation induced by the matrix is small as in very dilute aerogels.)

Hysteresis and scanning curves are manifestations of out-of-equilibrium behavior. This is well understood for instance in systems such as athermal martensites and low-$T$ ferromagnetic materials whose transformations are driven by an external field; these systems are well described by the $T = 0$ limit of models with quenched disorder [10] (models somewhat related to the lattice gas studied here). On the other hand, in the case of capillary condensation one often assumes that hysteresis is also the signature of a true equilibrium phase transition with two possible metastable states, gas and liquid, as in the standard van der Waals loop for bulk fluids and fluids confined in a single pore. However, this simple van der Waals picture fails for the present system because this latter has (in the region where capillary condensation occurs) a complex free-energy landscape with a large number of metastable states, as can be seen from studying the solutions of the local mean-field equation, Eq. (3). For each $T, \mu$ and each matrix realization, we have investigated 50 to 100 different initial conditions to Eq. (3). When plotted as in Fig. 3 on the $\rho_f - \mu$ diagram (for a typical matrix configuration of the $L = 48$ system), all solutions fall inside the major hysteresis loop that is found to coincide with the curves of extremal solutions obtained from an initially empty lattice (lower branch) and an initially filled lattice (upper branch).

The most significant finding of our study is that hysteresis occurs with as well as without an underlying equilibrium phase transition, the existence of this latter depending on the strength of the perturbation induced by the matrix. For a given matrix configuration we have computed the (approximate) equilibrium isotherms by taking at each $\mu$ the solution of the mean-field equations that gives the lowest $\Omega$. (We have also considered a weighted mean-field approach as in Ref. [13]: in all the cases studied here, the isotherms are virtually indistinguishable from that obtained by the first method.) For a large matrix-fluid interaction, e.g., for $y = 1.5$, there is no equilibrium phase transition, as can be seen in Fig. 3a where the equilibrium isotherm at $T^* = 0.8$ is perfectly smooth (it stays so at lower temperatures). On the other hand, in Fig. 3b, the same isotherm for $y = 1$ is discontinuous. This absence or presence of a true transition is supported by the finite-size scaling analysis presented in Fig. 4. For $y = 1.5$ the average equilibrium isotherm does not change with $L$ whereas it becomes steeper as $L$ increases for $y = 1$. In the latter case, the data can be fitted to the scaling form $\rho_f = a \tanh\{\beta L^\theta[\mu - \mu_t(L)]\} + b$ with $\theta \simeq 1.5$; indeed, in such an asymmetric model, the exponent $\theta$ characterizing a first-order transition in dimension

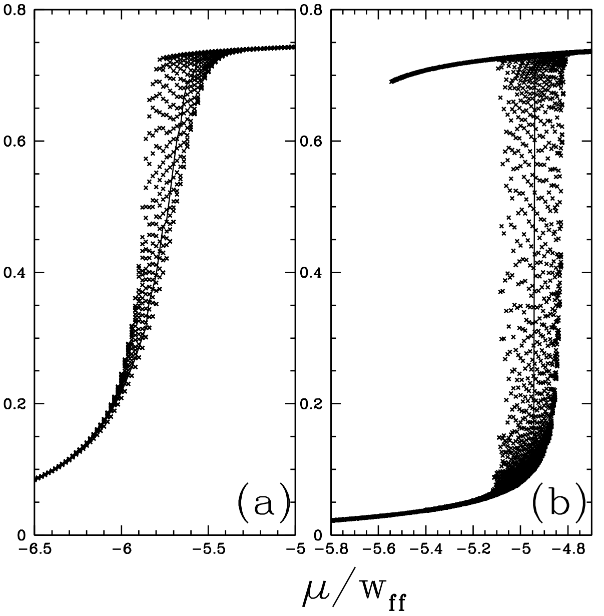

FIG. 3. Multiplicity of local mean-field solutions obtained from solving Eq. (3) at $T^* = 0.8$ with many different initial conditions for each value of $\mu$: (a) $y = 1.5$, (b) $y = 1$. The solid lines represent the equilibrium curves obtained by connecting the states of lowest grand potential.

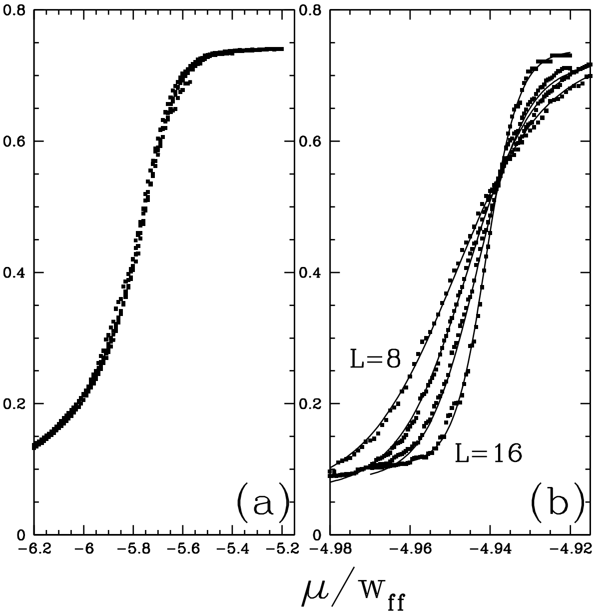

FIG. 4. Equilibrium isotherms for $T^* = 0.8$ and $L = 8$,10, 12, and 16: (a) $y = 1.5$, (b) $y = 1$. An average over 125 ($L = 16$) to 400 ($L = 8$) matrix realizations has been performed. In (b), the solid lines indicate the fit discussed in the text.

$d$ is $d/2$ instead of $d$ because $\mu$ at the transition in each realization fluctuates around its average value $\mu_t(L)$ with width $\delta\mu \sim L^{-d/2}$. (These results will be discussed in detail elsewhere [14].)

When the capillary critical point exists, it occurs at a $T$ significantly below the temperature $T_{\mathrm{hyst}}$ at which hysteresis first appears. This result is at odds with the behavior predicted for a fluid confined in a single pore [2,3] and is a consequence of the quenched disorder; on the other hand, the fact that true capillary criticality may still occur in disordered porous media is at odds with the prediction based on the independent-pore model [1,2,7] and results from the connectivity of the void space accessible to the adsorbed fluid.

The breakdown of the simple van der Waals picture of metastability in the present problem shows up distinctly when considering thermodynamic consistency along the sorption isotherms. Since the theory provides both the grand potential and the fluid density, one can study the validity of the Gibbs adsorption equation, $(\partial\Omega/\partial\mu)_T = -N\rho_f$, along particular isotherms. As shown in Figs. 5a, and 5b, the equation is not satisfied, neither along the adsorption isotherm nor along the desorption one. This results from the fact that the system often jumps from one grand potential minimum to another along these two isotherms and then loses thermodynamic consistency. An important consequence is that the thermodynamic integration procedure used for building equilibrium phase diagrams [2] is no longer valid for this model. For instance, in the case $y = 1.5$, this latter procedure predicts a capillary phase diagram whereas, as already discussed, no equilibrium phase transition takes place. We believe this may also be true more generally for other models of fluids in disordered porous materials. Note that the Gibbs adsorption equation is obeyed along the equilibrium isotherm, as illustrated in Fig. 5c.

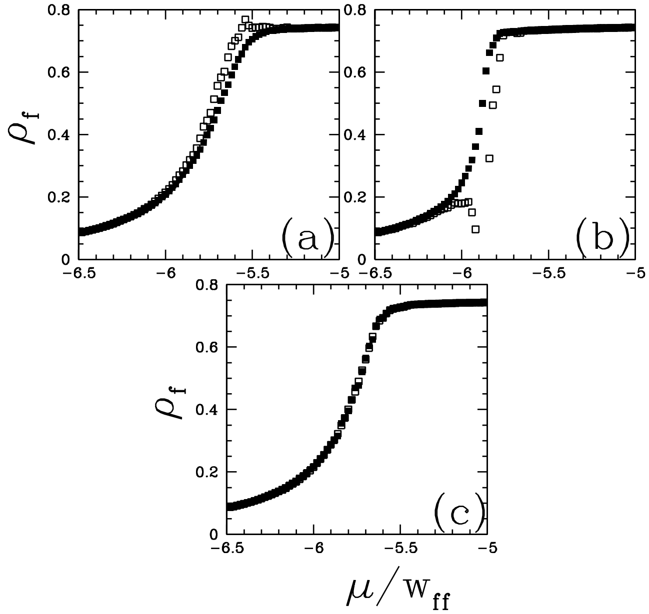

FIG. 5. Check of thermodynamic consistency $[(\partial\Omega/\partial\mu)_T = -N\rho_f]$ along the adsorption (a), desorption (b), and equilibrium (c) isotherms ($y = 1.5$, $T^* = 0.8$). Filled symbols: average fluid density obtained from the solution of Eq. (3). Open symbols: quantity obtained by differentiating the corresponding grand potentials.

As a final remark, we mention that the mean-field density functional theory also predicts the occurrence of out-of-equilibrium phase transitions similar to the macroscopic avalanches observed in low-$T$ ferromagnetic materials [10] (see the desorption isotherm in Fig. 1 for $T^* = 0.6$). Whether or not these transitions can be observed in capillary condensation of fluids in real mesoporous materials depends on the efficiency of the thermally activated processes.

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