Capillary condensation in disordered porous materials: hysteresis versus equilibrium behavior.

E. Kierlik\textsuperscript{1}, P. Monson\textsuperscript{2}, M. L. Rosinberg\textsuperscript{1}, L. Sarkisov\textsuperscript{2}, and G. Tarjus\textsuperscript{1}

\textsuperscript{1}Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France
\textsuperscript{2}Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA

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, thermodynamic consistency is not satisfied along the hysteresis loop, and out-of-equilibrium phase transitions are possible.

Capillary condensation of a gas inside a mesoporous material refers to the rapid change to a liquid-like state that occurs at a pressure (or chemical potential) lower than the bulk saturation value\textsuperscript{1} \textsuperscript{3}. 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\textsuperscript{2} \textsuperscript{3}. However, the situation in real mesoporous materials, such as porous glasses and silica gels, that consist of an interconnected network of winding 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\textsuperscript{3}, 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\textsuperscript{1} \textsuperscript{2} \textsuperscript{3}. 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. Indeed, in these systems that are locally heterogeneous, but macroscopically (statistically) homogeneous, the statistical-mechanical methods that have proved very efficient in dealing with bulk fluids and fluids in simple external fields, namely computer simulations, integral-equation theory and density functional theory, are plagued by many difficulties.

In this letter, we present a mean-field density functional theory of a disordered lattice-gas model. This model, introduced in a previous work\textsuperscript{3}, 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. (Note that the model could also be used to describe the demixing of binary mixtures in mesoporous materials\textsuperscript{2}.) 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\textsuperscript{1} \textsuperscript{2} \textsuperscript{3} 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, (iii) thermodynamic consistency is not satisfied along the hysteresis loop, and (iv) collective out-of-equilibrium phenomena such as macroscopic “avalanches” are possible.

The model is described by the following Hamiltonian,

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

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 could be considered\textsuperscript{3}, 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, \( y = w_{mf}/w_{ff} \), that determines the “wettability” of the matrix-fluid interactions \( \mu \) and we set \( \rho_m = 0.25 \). We use a 3D bcc lattice with linear size \( L = 8, 12, 16, 24, 48 \) for which we consider many different configurations of the random matrix, from 1400 for \( L = 8 \) to 5 for \( L = 48 \). Most of the results are illustrated here for \( L = 48 \) and typical matrix configurations, but when necessary, e.g., to check the existence of phase transitions, we have performed a finite-size analysis after averaging over all 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 \( \{ \eta_i \} \):

\[
F(\{ \rho_i \}) = \frac{1}{\beta} \sum_i [\rho_i \ln \rho_i + (\eta_i - \rho_i) \ln (\eta_i - \rho_i)]
- w_{ff} \sum_{<ij>} \rho_i \rho_j - w_{mf} \sum_{<ij>} [\rho_i (1 - \eta_j) + \rho_j (1 - \eta_i)],
\]

where \( \beta = 1/(k_B T) \) and \( \rho_i = < \eta_i \tau_i > \) 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 \( \Omega(\{ \rho_i \}) = F(\{ \rho_i \}) - \mu \sum_i \rho_i \) w. r. t. the \( \rho_i \)'s provides the grand potential \( \Omega \) of the adsorbed fluid. The corresponding equations for the fluid density on each site are

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

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, \( \Delta \mu = 10^{-3} \)) and (2) to search more exhaustively the solutions of Eq. (3) for a given \( \mu \), we repeat the iteration procedure with a large number of initial conditions (typically, \( 10^5 \)) 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] [3], with an asymmetric hysteresis loop (corresponding to the H2 shape in the IUPAC classification) characterized by a step descent branch and a smoothly increasing adsorption branch. The so-called “hysteresis phase diagrams” that are constructed from the points at which the loop opens and closes are shifted to lower \( T \) and higher \( \rho_f \) compared to the bulk-fluid coexistence curve, and their (asymmetric) shape is also quite comparable to what is obtained from experimental data [1] [2] [3].

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 [4]. It has been stressed that these curves are not properly reproduced by the widely used independent-pore model [1] [2] [3] [4]. 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 that display the “return-point memory” effect, in close analogy to the hysteretic behavior displayed by a variety of systems [1] [2] [3] [4].

The above results confirm that the present approach reproduces qualitatively the phenomenology associated with capillary condensation in porous glasses and silica gels. This indicates that, despite its simplicity, the model 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

FIG. 1. Theoretical sorption isotherms for \( y = 1.5 \) at \( T = 0.6, 0.8, 0.95, 1.1 \) and 1.25. (The mean-field bulk critical point is at \( T = 2 \).)
FIG. 2. Theoretical desorption (a) and adsorption (b) scanning curves for \( y = 1.5 \) and \( T = 0.8 \).

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 like 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 equations, 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). We suspect that this picture corresponds to the situation encountered in real disordered porous materials (a similar behavior has been observed for other disordered microstructures \([8]\)).

The most significant finding of our study is that hysteresis associated with capillary condensation in disordered porous media 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. We have computed the equilibrium properties of the model by means of the weighted mean-field approach \([13]\): at each \( \mu \) and \( T \), densities of extensive quantities such as the fluid density \( \rho_f \) are calculated as Boltzmann weighted sums over the different solutions of the mean-field equations (i.e., each solution \( \alpha \) is weighted by \( e^{-\beta\Omega_\alpha} / \sum_\alpha e^{-\beta\Omega_\alpha} \)). The average over the various matrix realizations is taken afterwards. For a large matrix-fluid interaction, e.g., for \( y = 1.5 \), there is no equilibrium phase transition: this is illustrated in Fig. 3a where the equilibrium isotherm at \( T = 0.8 \) is perfectly smooth (it stays so at lower temperatures). On the other hand, for \( y = 0.5 \), the system undergoes a true thermodynamic transition at low \( T \) as it becomes isomorphic to the site-diluted Ising model \([9]\) (\( \rho_m = 0.25 \) is above the percolation threshold). For the intermediate value \( y = 1 \), equilibrium isotherms may display steep portions, as illustrated in Fig. 3b for \( T = 1 \) (however, a finite-size scaling analysis of the results for \( L = 8, 12 \) and 16 seems to indicate that this isotherm is still supercritical). The capillary critical point certainly occurs at a \( T \) significantly below the temperature \( T_{hyst} \) at which hysteresis first appears. This result is at odds with the behavior predicted for a fluid confined in a single pore \([3]\) 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\cite{1} and results from the connectivity of the void space accessible to the adsorbed fluid.

![Graph](image)

FIG. 4. Check of thermodynamic consistency \((\partial \Omega/\partial \mu)_{\text{T}} = -N \rho_f\) along the adsorption (a), desorption (b), and equilibrium (c) isotherms \((y = 1.5, T = 0.8)\). Filled symbols: average fluid density obtained from the mean-field solutions. Open symbols: quantity obtained by differentiating the corresponding grand potentials.

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, \((\partial \Omega/\partial \mu)_{\text{T}} = -N \rho_f\), along particular isotherms. As shown in Fig. 4, a,b, 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 a given grand potential minimum to another along these two isotherms and then looses thermodynamic consistency. An important consequence is that the thermodynamic integration procedure used for building equilibrium phase diagrams\cite{7} 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. 4c. (Interestingly, in the cases studied here, the isotherm calculated from the weighted mean-field approach is virtually indistinguishable from that obtained by taking at each \(\mu\) the solution with the lowest grand potential.)

As a final remark, we mention that the mean-field density functional theory also predicts the occurrence of out-of-equilibrium phase transitions. Similarly to the macroscopic avalanches observed in low-\(T\) ferromagnetic materials\cite{2}, the adsorption and desorption branches of the major hysteresis loop may display sharp jumps. This is illustrated in Fig. 1 where one can see that the desorption isotherm has a discontinuity at the lowest temperature shown. Due to the asymmetry of the random chemical potentials exerted by the matrix on the fluid, the jump always occurs at a higher \(T\) in the desorption branch than in the adsorption branch. Whether or not this out-of-equilibrium transition, with its associated critical behavior\cite{10}, 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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