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The Physics of Capillary Condensation in Disordered Mesoporous Materials: A Unifying Theoretical Description

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Abstract. We present a unifying theoretical approach of capillary condensation in disordered mesoporous materials. It provides a comprehensive picture of this phenomenon that accounts for processes occuring on all length scales and clarifies the relation between hysteretic and equilibrium behavior. The shape of the hysteresis loop is shown to depend on the presence or absence of out-of-equilibrium phase transitions, whose nature differs on adsorption and on desorption.

Keywords: capillary condensation, hysteresis, disordered solids

1. Introduction

Despite its widespread use for characterizing mesoporous materials, the phenomenon of capillary condensation is still debated and interpreted in a variety of ways often at odds with each other. Part of the confusion comes from the fact that *disorder* (both geometric and energetic), which charaterizes materials such as porous glasses and gels, brings about new physics that makes the well-established theory of capillary condensation in single pores or in ordered porous materials not transferable. As a result, there are a number of very basic points whose consequences have often not been fully appreciated; these points involve considerations of time scales and length scales.

Consider first the time-scale problem. The signature of what is known as "capillary condensation" is a hysteresis in the adsorption/desorption isotherms (Gregg and Sing, 1982; Rouquerol et al., 1999). By its very nature, hysteresis means that the observed phenomenon is *out of equilibrium*. The fact that the location and the shape of the hysteresis loop are reproducible in experiments indicates that the observation time is larger than fast, local equilibration processes, but is smaller than the time for reaching true, global equilibrium; this latter time may indeed be extremely large in the regime of interest, like in the case of glassy liquids and polymers below their glass tranformation temperature. This out-of-equilibrium character can be benign as in the liquid/gas transition in bulk fluids or fluids in single pores (Evans, 1990): there, the system can be trapped in a metastable phase that can be described by extending equilibrium concepts and relations. The situation, however, is radically different in the presence of externally imposed disorder. This is well known from the study of "dirty" magnetic systems with impurities (Fisher et al., 1988): disorder generates a very large number of metastable states (possibly exponentially large in the size of the system) in which the system can get trapped, states that are not describable by a thermodynamic-like approach.

The second issue concerns length scales. Disordered mesoporous materials contain a highly interconnected, irregular, 3-dimensional pore space made of cavities or "pores" with various shapes and sizes (Gelb et al., 1999). Preferential adsorption and formation of a liquid layer on the solid occur at a molecular or "microscopic" scale, filling or emptying of cavities (pores) may involve "mesoscopic" scales, but the *3-dimensional nature* of the void space also allows truly collective

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processes at a "macroscopic" scale. The latter are completely neglected in the traditional approaches that describe the solid as a collection of independent pores of well-defined geometry (cylinders, slits or ink-bottles).

We have developed a statistical mechanical approach that provides a unifying framework for describing the cooperative processes at work in capillary condensation of gases in disordered mesoporous solids (Kierlik et al., 2001; Rosinberg et al., 2003; Detcheverry et al., 2003). The main conclusions are as follows:

(1) Contrary to the van der Waals picture of metastability, hysteresis may occur even in the absence of an underlying equilibrium phase transition. As a consequence, the disappearance of hysteretic behavior does not correspond to a capillary critical point.

(2) Collective effects at a macroscopic level may lead to out-of-equilibrium phase transitions that are different on adsorption and on desorption; the presence or absence of such transitions, as well as their nature, determine the shape of the hysteresis loop (H1 versus H2, as seen in Fig. 1) and the characteristics of the scanning curves and other subloops obtained for various histories of the applied pressure or chemical potential.

(3) Adsorption is always a bulk phenomenon whereas desorption may involve the interface between the solid and the gas reservoir.

(4) The mechanisms for adsorption and for desorption change as one varies temperature or the physical characteristics of the system. In the case of desorption for instance, different mechanisms occur when decreasing the temperature or the wettability of the solid/fluid interface, or increasing the porosity: (i) cavitation (formation of gas bubbles in the bulk of the material); then, (ii) percolation (with the invasion of the solid by a 3-dimensional

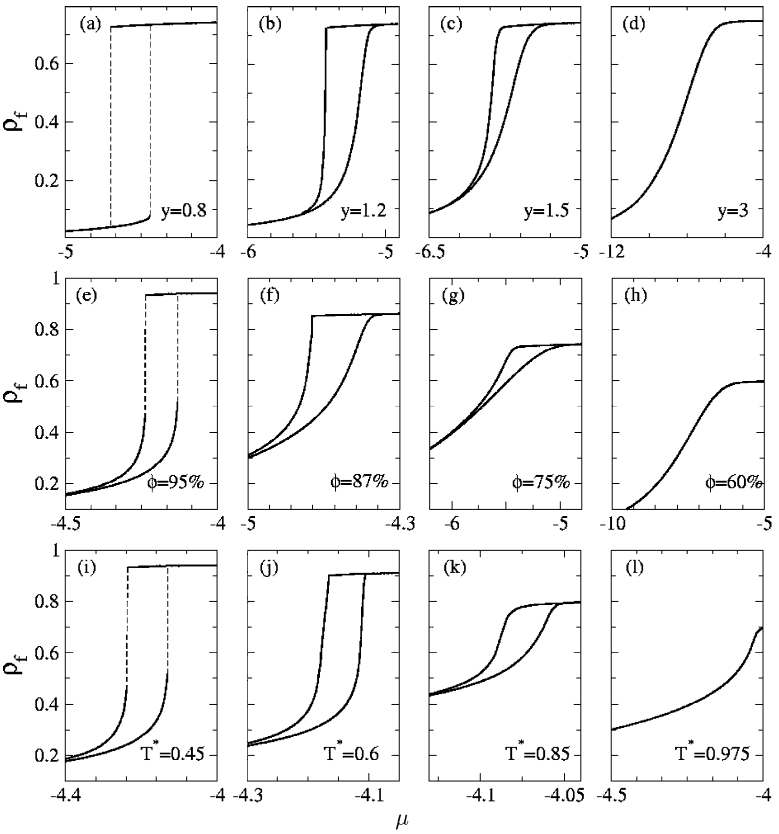

Figure 1. Theoretical adsorption/desorption hysteresis loops in two models of disordered porous solids: upper row, random matrix ($\phi = 75\%$, $T^* = T/T_c^{\text{bulk}} = 0.4$); other rows, DLCA aerogels (middle: $y = 2$, $T^* = 0.45$; bottom: $y = 2$, $\phi = 95\%$). Bulk gas-liquid coexistence occurs at $\mu = -4$.

self-similar cluster of gas that produces a cusp in the isotherm); and finally, (iii) in high-porosity solids such as very light aerogels (Tulimieri et al., 1999), a depinning transition (with the sudden passage of a compact gas-liquid interface that induces a vertical step in the isotherm). Contrary to the pore-blocking description, percolation comes as only one of the possible mechanisms for draining and is self-generated with no need for specific kinetic constraints.

(5) Cooperative processes on all scales, which physically correspond to condensation or evaporation events occuring at a given chemical potential (pressure), can be generically described in terms of *avalanches*. An avalanche need not correspond to the filling or emptying of a given "pore", but may involve a domain (gas bubble or liquid droplet) that extends over several such "pores". As a result, determining a pore size distribution via analysis of an isotherm (Gregg and Sing, 1982; Rouquerol et al., 1999) may, even in the absence of collective processes on a macroscopic scale, be meaningless, beyond the mere estimate of some typical size.

2. Theory and Results

A complete theoretical description of adsorption of fluids in disordered porous materials, from micro- to macroscopic scales, is out of reach. To make the problem tractable while retaining the salient physical ingredients, we introduce two simplifications, the first one related to the treatment of length scales, the second to that of time scales.

First, we use a *coarse-grained* description of the solid/fluid system, in which the elementary unit is the size of a composite particle forming the solid (typically a few nanometers); on this scale a cell represents a significant volume of fluid. This allows to introduce a lattice-gas model in which molecular details are incorporated in some effective parameters. The model retains the most important features of the system, the 3-dimensional structure of the solid matrix, the variable "wettability" of the solid by the fluid, the exclusion and confinement effects, and the disorder generated by the solid.

Secondly, we neglect the effects of thermal fluctuations. This is expected to be of minor importance as far as the static or "thermodynamic" properties are concerned because disorder-induced fluctuations, which we fully account for, play a dominant role. In the dynamics, this amounts to neglecting the thermally activated processes by which the system may "escape" from a metastable state and ultimately reach true equilibrium. Our assumption is that those processes are slow compared to the the experimental time scale. In our description the system moves from one state to another only under the action of the external drive, i.e., a change in the pressure P or, equivalently, in the chemical potential μ.

The starting point of the analysis is the following expression of the grand-potential functional in the local mean-field approximation (Kierlik et al., 2001):

$$\begin{aligned}\Omega[\{\rho_i\}, T, \mu] &\\ = k_B T \sum_i [\rho_i \ln \rho_i + (\eta_i - \rho_i)\ln(\eta_i - \rho_i)]&\\ - w_{ff} \sum_{<ij>} \rho_i \rho_j - w_{sf} \sum_{<ij>} [\rho_i(1-\eta_j)&\\ + \rho_j(1-\eta_i)] - \mu \sum_i \rho_i & \qquad (1)\end{aligned}$$

where ρ_i is the thermally averaged fluid density at site i ($i = 1 \ldots N$) and $\eta_i = 0, 1$ is a quenched variable describing the occupation of the lattice by the solid "particles" ($\eta_i = 0$ if the site is occupied by the solid). The η_i's are sampled from a given distribution that describes the structure of the solid: in the following, we consider a purely random distribution and a model aerogel generated by a diffusion-limited cluster aggregation (DLCA) algorithm; other distributions representative, e.g., of silica xerogels or Vycor glass (Sarkisov and Monson, 2001; Kikkinides et al., 2003) can be used as well. w_{ff} and w_{sf} denote the fluid-fluid and solid-fluid attractive interactions, respectively, and the double summations run over all distinct pairs of nearest neighbour sites. The solid porosity is given by $\phi = (1/N)\sum_i \eta_i$ and the ratio $y = w_{sf}/w_{ff}$ controls the wettability of the solid surface. Minimizing Ω with respect to ρ_i at fixed T and μ for a given realization of the solid (i.e., a given set $\{\eta_i\}$) yields N coupled equations that are solved by iteration. Sorption isotherms $\rho_f(T, \mu) = (1/N) \sum_i \rho_i$ and scanning curves are obtained by changing μ in small steps $\delta\mu$. Equilibrium curves are obtained by searching for the most stable among all possible solutions at a given μ, a computationally very demanding task.

More details can be found in our previous publications (Kierlik et al., 2001; Rosinberg et al., 2003; Detcheverry et al., 2003). However, we would like to

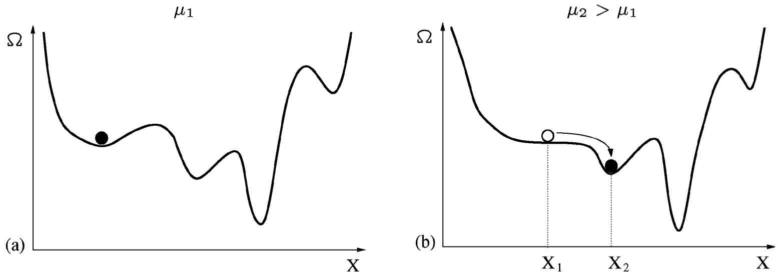

Figure 2. Schematic one-dimensional cartoon of the grand potential landscape for two different chemical potentials (x denotes some arbitrary coordinates in the N-dimensional space). For $\mu_2 > \mu_1$, the state in which the system is trapped (filled circle) becomes unstable and the system falls into a new minimum. The discontinuous passage from x_1 to x_2 that is associated to a local "spinodal" defines an avalanche.

stress a few methodological points: (i) as for all systems with quenched disorder, one must average the results over a significant number of realizations of the solid (depending on the system size); (ii) the presence or not of phase transitions can only be determined by a finite-size analysis that requires studying several lattice sizes; and (iii) finally, boundary conditions matter because the presence of a physical interface between the solid and the gas reservoir (as in experiments) may determine the draining process.

Our results are illustrated in Fig. 1 that shows the variations of the adsorption/desorption isotherms as one changes either the temperature T, the porosity ϕ, or the interaction ratio y. The main features are discussed in the introduction. It should be stressed that contrary to the common lore in the field of adsorption, a hysteresis loop with steep branches, as in Figs. 1(a), (e), and (i), does not automatically imply a narrow distribution of pore sizes: this is clearly not true for the 95% aerogel ! In disordered materials, such a H1-type loop results from fully 3-dimensional collective processes that take place at low enough temperature and high enough porosity.

3. Cooperative Processes on Mesoscopic Scale: Avalanches

As we have already pointed out, cooperative processes may occur on all scales, either on adsorption (condensation events) or on desorption (evaporation events). If one considers the hypersurface formed by the grand potential functional $\Omega[\{\rho_i\}]$ as a function of the local fluid densities as a "landscape", such processes correspond to the sudden passage from one metastable state (i.e., a local minimum of Ω) to another one when the former becomes unstable due to a small change in μ: this is schematically illustrated in Fig. 2; the associated jump in the landscape is a cooperative process that one defines as an "avalanche".

Whether or not these avalanches are experimentally observable depend on their size, since submacroscopic avalanches are not detectable in the average fluid density in the thermodynamic limit (see however Lilly and Hallock, 2001). In our theoretical study performed with finite-size systems, avalanches can be identified and analyzed even when they remain at a mesoscopic scale, which is the case at high enough T or strong influence of the solid. Avalanches allow to define precisely the filling or the emptying of "domain", even if the material cannot be described as a collection of independent pores.

As illustrated in Fig. 3 in the case of a 95% aerogel, domains involved in avalanches need not conform to any simple geometry. (In the figure, only the regions that contribute to these mesoscopic condensation events are shown.) Moreover, domains are not necessarily similar upon filling and draining. Even though

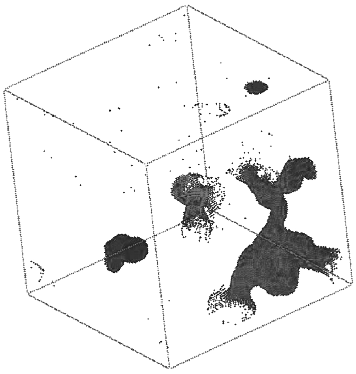

Figure 3. Illustration of a few avalanches in a 95% aerogel at the end of the filling process ($y = 2$ and $T^* = 0.85$).

the overall location of the hysteresis loop correlates reasonably well with an average length characteristic of the solid (see for instance the displacement of the loop as a function of porosity in Fig. 1), distributions of pore size extracted from analysis of sorption isotherms in disordered mesoporous solids do not seem to have any clear meaning.

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