

A Model of Hysteresis in Narrow Pores.

U. MARINI BETTOLO MARCONI(*) and F. VAN SWOL(**)

(*) *Dipartimento di Fisica, II Università di Roma «Tor Vergata», 00173 Rome, Italy*

(**) *Chemical Engineering Department, University of Illinois
1209 West California Street, Urbana, IL 61801, U.S.A.*

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Abstract. – We introduce a new model of adsorption hysteresis that takes the formation of a meniscus explicitly into account by allowing the density to vary in the direction parallel to the walls. We apply the new geometry to a lattice gas model and solve the self-consistent equations for the density profile in the mean-field approximation. Adsorption is similar to that in single, infinitely long pores. Desorption is qualitatively different: a meniscus forms at the pore ends and subsequently recedes. Our results justify recent assumptions made about the nature of hysteresis.

Significant progress has recently been made in understanding fluid phase behaviour in mesoporous solids from a molecular point of view. In particular, the physics underlying the phase transitions in an idealized infinitely long pore has been elucidated by employing mean-field density functional theory (DFT) methods [1]. The theory quite accurately predicts capillary condensation. That is, it locates the undersaturated bulk pressure (or chemical potential) at which a gaslike state coexists with a liquidlike state. Moreover, by using the most refined version of DFT, namely, the smoothed density approximation (SDA) introduced by Tarazona [2], an accurate description of fluid structure is obtained that is in excellent agreement with recent simulations [3, 4].

In spite of these successes the theory of single, infinitely long pores does not seem to give a complete account of the experimental adsorption isotherms. Experimentally one generally observes a hysteresis loop [5]. The adsorption branch rises steeply at a pressure which is higher than that of the desorption branch. The interpretation is that the states along the adsorption branch are not represented by stable states but instead are thought to be metastable corresponding to a local minimum in the grand potential, since they are beyond the thermodynamic transition point. This idea goes back to Cassell [6] and was subsequently explored in more detail by Hill [7]. Similarly, for pressures less than the condensation pressure the states along the desorption branch are only metastable. Metastable states naturally arise in the mean-field theory and the theory appears to give a proper account of the adsorption process. However, it fails to give a realistic account of desorption. Namely, if

the confined fluid were to follow the metastable branch until it reached the spinodal one would find that the extent of the loop toward lower pressures is significantly over-estimated [8-10].

Other explanations that have been put forward to explain hysteresis loops are purely macroscopic, based on the instability of an adsorbed film [9], and can be traced back to the work by Cohan [11]. All of these are based on a thermodynamic approach that makes use of the Kelvin equation to locate the transition. The Kelvin equation describes the equilibrium of vapour and liquid phases that meet at a curved interface, *i.e.* at a meniscus. The difference in adsorption and desorption is then related to a difference in shapes of the meniscus, in particular to a different radius of curvature. A vast literature exists on this subject and the model envisioned by Cohan [11] enjoys a great popularity (*e.g.*, see ref. [12]). However, it is well known that the notions underlying this approach, such as a sharp interface, uniformity of the two fluid phases and the use of a planar surface tension are untenable when the pores are small on a molecular scale. Hence we have to resort to a microscopic approach and use statistical mechanical concepts. Finally, we note that metastability in a *single* pore is not the only possible explanation for adsorption hysteresis. In particular, Mason [13] has put forward a pore blocking model that concentrates entirely on the connectivity of a pore network and assumes *reversible* adsorption in the individual pores.

In this letter we propose a new model that explicitly takes the finite length of a single pore into account, and hence a meniscus is allowed to form. No such calculation exists at present, although the liquid-vapour equilibrium in confined geometries has been studied extensively. Our approach employs the same density functional methods that were successful in related areas and in locating capillary condensation. To anticipate the main result, on the basis of our self-consistent equations we are now able to justify the desorption behaviour that had previously been merely postulated by Cole and Saam [9], and more recently by Ball and Evans [8]. The presence of an interface at the end of a filled pore is crucial in the desorption process. No significant metastability occurs upon emptying the pore by reducing the chemical potential. Instead, the meniscus gradually recedes, thus lowering the adsorption.

In order to allow for the formation of a meniscus separating the two phases one has to break the symmetry parallel to the walls (in a slitlike pore) or in the direction of the pore axis (in a cylindrical pore). Here we will restrict ourselves to slitlike pores consisting of two parallel plates (walls). The plates are rectangular with an infinite edge in one direction (x) ($L_x \rightarrow \infty$) and a finite edge L_y in the remaining one (y). The finite direction mimics the pore-ends that were previously ignored. We considered two types of finite pores. Model A is an open slit, with both ends open. Model B we refer to as a closed slit: one end is open and the other is closed. The latter model is representative of a wedge-shaped pore. In order to investigate the new symmetry we focused on the lattice gas model. Although this is not a realistic model for continuum fluids it does exhibit all the qualitative features that are important to capillary condensation [14] and, in addition, the single wall has been studied in detail [15, 16].

Consider a lattice gas between two parallel walls each with dimensions L_x ($L_x \rightarrow \infty$) and L_y which are separated by a distance L_z . The sites are arranged on a simple cubic lattice. The external field W , due to a single wall, varies only in the y and positive or negative z directions. A wall is considered to consist of filled lattice sites that extend infinitely in the x and positive or negative z directions. Each wallsite interacts with a pore-site via a r^{-6} interaction and the total external potential at a position (y, z) is

$$W(y, z) = -\varepsilon \frac{3}{8} \pi \alpha \sum_{k=1}^{L_y} \sum_{l=1}^{N_z} \{ [(y/\sigma - k)^2 + (z/\sigma + l)^2]^{-5/2} + [(y/\sigma - k)^2 + (z/\sigma + l - L_z)^2]^{-5/2} \}, \quad (1)$$

where σ is the unit of length, α is a parameter that controls the wall strength and $N_z \sigma$ is the plate thickness. For the open pore the walls and the lattice gas on both ends are extended in the y direction by L_b sites (see also fig. 2). These sites represent the reservoir and the walls surrounding it consist of sites with an average occupancy set equal to that of the bulk gas. For the closed pore, we have a reservoir at one end and a plate similar to (1) that closes off the opposite end. The Hamiltonian can then be written as

$$H = -\varepsilon \sum_{\langle jkl, j'k'l' \rangle} n_{jkl} n_{j'k'l'} + \sum_{\langle jkl \rangle} W(y_k, z_l) n_{jkl} + H_{\text{res-bound}}, \tag{2}$$

where $n_{jkl} = 1$ (or 0) if the site is occupied (or empty) and $\varepsilon (> 0)$ characterizes the site-site interaction. The first summation runs over nearest neighbours of the subsystem pore fluid + reservoir fluid. The second summation runs over all the sites of the subsystem and the last term represents the nearest-neighbour interaction of the fluid sites with the reservoir boundaries. The mean-field solution is obtained by minimizing the grand potential functional with respect to the average occupancies ρ_{kl} . The expression for Ω/L_x (the grand potential per unit length in the x -direction) is a straightforward generalization of the planar mean-field functional [15, 14], and the resulting Euler-Lagrange equations are solved iteratively in a similar manner. In the calculations we varied the temperature, the height of the plates (L_y), separation (L_z) and the strength of the external field (*i.e.* α).

In fig. 1 we present typical results for $\alpha = 4.512$, $T/T_c = 0.8$ and a plate separation of 18 layers. The infinite pore (fig. 1A)) shows very extended loops as reported previously [14].

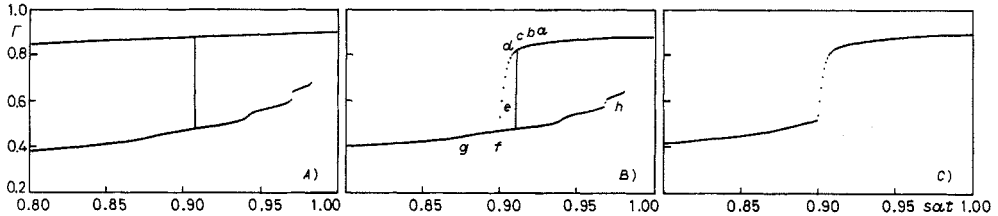


Fig. 1. - Adsorption Γ vs. saturation parameter «sat» (defined in the text) for a plate separation $L_z = 18$, a pore length $L_y = 140$, $T/T_c = 0.8$ and $\alpha = 4.512$. The phase transition is marked by a solid line. A) The infinite pore. B) The open pore. The labelled points are shown in fig. 2. C) The closed pore, one end is open and one end is closed.

The phase transition takes place at a value of the saturation parameter «sat» (defined as $\rho/\rho_{\text{sat}}(\text{gas})$) which is close to 0.907. The «liquid» branch terminates at a point which is slightly shifted from the bulk mean-field spinodal due to the finite L_z . Up to this point the states correspond to a local minimum of the grand potential. The adsorption branch also displays metastable states. The coverage $\Gamma \equiv 1/(L_y \cdot L_z) \sum_{k=1}^{L_y} \sum_{l=1}^{L_z} \rho_{kl}$, grows continuously and is nearly

vertical when the loop closes at a «sat» value close to 1. The results for a finite open pore (model A) are shown in fig. 1B) for pore length $L_y = 140$ (the ratio L_y/L_z is very close to that of ref. [10]). The adsorption branch is nearly identical to that of the finite pore shown in fig. 1A). In contrast, the desorption branch shows a novel feature: the loop rounds off and rapidly starts dropping at a value close to the transition. It decreases steeply in a (almost) continuous fashion until it eventually merges into the adsorption branch. The transition itself, which follows from the equality of the grand potentials of both branches, takes place inside the loop at a «sat» value slightly larger than that of the infinite pore. This shift is due

to a finite size correction that for large systems is of order L_z/L_y . The results for the closed pore (model B) are plotted in fig. 1C), the isotherm does not exhibit any hysteresis. This is in agreement with the macroscopic picture (*e.g.*, ref. [12]), where wedge shaped pores show smoothly increasing isotherms. It is worthy of note that the first part of the desorption is nearly identical to that of the open pore. It is only near the end of the steep decrease that the two models differ, the closed pore showing a slightly smoother isotherm. In the open pore the «liquid» configuration eventually becomes unstable and shows a small jump to the «gas». It is perhaps worth stressing that the desorption behaviour that we observe for the open-ended pore is entirely due to the symmetry breaking induced by the ends and is *not* merely a consequence of the finite length L_y . In other words even in the limit $L_y \rightarrow \infty$ will we observe the behaviour shown in fig. 1B) (and *not* that of fig. 1A)), the topology of the pore being the essential factor.

It is instructive to examine the full density profiles ρ_{kl} , for the open pores. In fig. 2 we display the results for selected state points along the isotherm shown in fig. 1B). We have plotted the contour $\rho = 0.5$, which is obtained by interpolation in the matrix ρ_{kl} . The contours clearly show the mechanism by which a narrow pore empties (fig. 2A)). The liquid-filled pore has a meniscus (labelled «a») which for this particular value of «sat» happens to be concave.

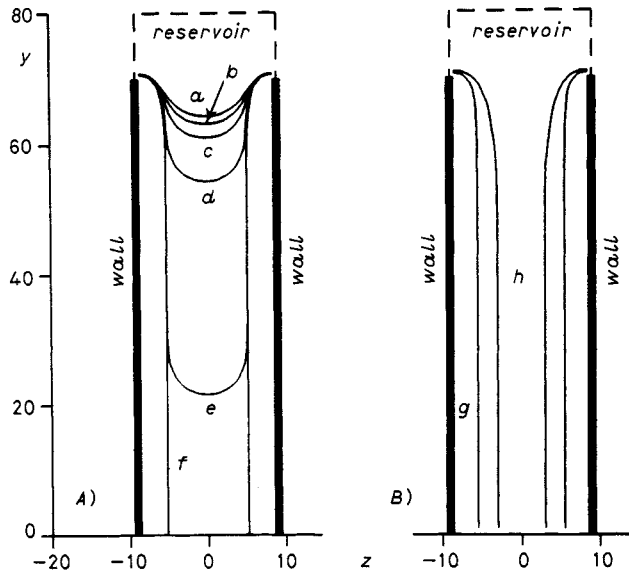


Fig. 2. - Menisci in an open pore for a series of «sat» values. The labelling corresponds to that of fig. 1B). The labelled solid curves are contour lines ($\rho = 0.5$) drawn in the matrix of densities ρ_{kl} . The thick lines indicate the position of the wall. The dashed lines denote the boundaries of the bulk (gas) region. Only the top half of the pore is shown. A) desorption, B) adsorption.

As «sat» is lowered the meniscus gradually changes shape, *i.e.* the radius of curvature decreases. This corresponds to the rounding part of the desorption branch (see fig. 1B)). Eventually the meniscus merely recedes at an increasing rate until it finally becomes unstable and a small jump takes place to a «gas» configuration. At this point the hysteresis loop is closed. Along the adsorption branch the thickness of the adsorbed layer steadily increases with «sat» (fig. 2B)). At the end of this branch, the film becomes unstable with respect to meniscus formation [9]. Hence at this point the density profile changes its symmetry. The subsequent filling of the pore is extremely rapid since we are already well

beyond the thermodynamic transition, and essentially what is observed is a large jump to a «liquid» configuration. As a result this part of the isotherm is very similar to that of the infinite pore. The desorption behaviour of the closed pore is very similar to that of the open pore, but the adsorption clearly differs. For a closed pore this size and at this temperature the isotherm is reversible. A more detailed discussion of the receding meniscus will be published elsewhere [17].

We conclude that the novelty of our approach, simply allowing two phases to be present simultaneously and in direct contact, for the first time provides a complete picture of hysteresis in single uniform pores. In particular, the shape of the desorption branch is a reflection of the nucleation process that is initiated by the pore ends. This is a clear improvement over the earlier microscopic descriptions [1] dealing with infinite pores, which linked the desorption behaviour to the existence of a spinodal that terminated the metastable liquid branch.

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