

Capillary condensation, invasion percolation, hysteresis, and discrete memory

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A model of the capillary condensation process, i.e., of adsorption-desorption isotherms, having only pore-pore interactions is constructed. The model yields (1) hysteretic isotherms, (2) invasion percolation on desorption, and (3) hysteresis with discrete memory for interior chemical potential loops. All of these features are seen in experiment. The model is compared to a model with no pore-pore interactions (the Preisach model) and to a related model of interacting pore systems (the random field Ising model). The capillary condensation model differs from both. [S0163-1829(96)06725-2]

I. INTRODUCTION

Hysteresis is often seen in a measured quantity's response to a probe. For example, the displacement $u(t)$ response of an oscillator to a periodic driving force $F(t)$ is hysteretic. In this case the hysteresis in u versus F is due to a damping induced phase difference between $u(t)$ and $F(t)$. Hysteresis with discrete memory (H/DM) is less familiar although it is seen in a wide variety of physical and model systems.¹⁻⁵ Discrete memory or end point memory refers to the memory and memory erasure that occur at the extrema of the probe protocol. In magnetism the probe is the external field; in capillary condensation the probe is the chemical potential. A very restricted set of hysteresis models also have discrete memory. An elegantly simple explanation of H/DM is given by the Preisach model,⁶⁻⁸ a model for the behavior of a large number of noninteracting, individually hysteretic units.

In many instances where the Preisach model is used the basic condition for its application, noninteraction or independence, is absent. For example, the Preisach model has been extensively used to describe the capillary condensation process, i.e., adsorption-desorption isotherms.⁹ However, the invasion percolation feature seen in many isotherms⁴ provides compelling evidence for pore-pore interactions and suggests that a Preisach model has circumscribed validity.^{10,11}

More sophisticated models have been developed for adsorption-desorption isotherms^{12,13} and for systems that possess H/DM.¹⁴ The purpose of this note is to describe a capillary condensation model (CCM) that, in marked contrast to the Preisach model, owes all of its behavior to the interaction of individually nonhysteretic units, and to show that this model possesses H/DM. The CCM possesses the essential features necessary to give the desired qualitative behavior of adsorption-desorption isotherms although it has been stripped of much of the detail that would make it a practical model for inverting data to learn the pore space geometry. In Sec. II the capillary condensation model is described. In Sec. III results of numerical simulation of the CCM are presented. The essential content of the CCM and its relationship to other models, e.g., the random field Ising model, are discussed in Sec. IV.

II. MODEL

The capillary condensation process is characterized by the geometry of the pore space, the rules for the evolution of fluid configurations in the pore space, and by the chemical potential protocol to which the fluid is subjected. For definiteness and simplicity we adopt the following model.

(a) The pores, cylinders of length b , are the bonds of a square lattice $L \times L$. There are $N = 2 \times (L/b)^2$ pores.

(b) The pores are in the presence of a fluid at chemical potential μ , i.e., the pore space is connected to a chemical potential reservoir.

(c) A pore is either empty, in state $\sigma = 0$, or filled with fluid, in state $\sigma = 1$. A pore in state 0 has a thin liquid film on its surface and vapor in its interior. A pore in state 1 is filled with liquid and may have a meniscus at its ends depending on the state of its near neighbors (the six pores with which it shares a node).

(d) To the i th pore we assign a radius r_i from the probability density $\rho(r)$ and a critical value of the chemical potential ϕ_i from the probability density $\tau(\phi)$. There may be a correspondence between ϕ_i and r_i so that

$$\rho(r)dr = \tau(\phi)d\phi. \quad (1)$$

To avoid details that depend on $\rho(r)$ and $\tau(\phi)$ but are inessential to our discussion we map the spectrum of critical pore chemical potentials onto the interval $[0,1]$ by ordering ϕ_1, \dots, ϕ_N from smallest to largest and using $p_i = (\text{ordinal number of } \phi_i)/N$. We map the reservoir chemical potential to the appropriate point in the sequence p_1, \dots, p_N and continue to denote it as μ .

(e) The fluid in the system is carried through a chemical potential protocol $\mu(t)$. Here t simply indicates that the chemical potential evolves in time. This time evolution occurs so slowly that the fluid configurations in the pore space are taken to be a sequence of stable or metastable fluid configurations $C(t) = C(t_m) = C_m$ consistent with the chemical potential protocol, $\mu(t) = \mu(t_m) = \mu_m$.

(f) On chemical potential increase $\mu_{m+1} > \mu_m$. If $\mu_m < p_i < \mu_{m+1}$, then $\sigma_i = 0 \rightarrow 1$.

(g) On chemical potential decrease $\mu_{m+1} < \mu_m$. If $\mu_{m+1} < p_i < \mu_m$, and

$$\nu_i \equiv -z + \sum_{j=1}^z \sigma_j < 0, \quad (2)$$

then $\sigma_i = 1 \rightarrow 0$, where the sum on j is over the z near neighbor pores (bonds) that share a node with pore i . A pore will empty if the external chemical potential is less than the pore's critical value of the chemical potential *and* if at least one neighboring pore is empty. This rule yields the invasion percolation process.¹⁰

The rules (f) and (g) differ by the involvement of the access field ν_i . As the pores are filling they make the transition $\sigma_i = 0 \rightarrow 1$ regardless of the condition of the neighboring pores. The reason for the simplicity of this rule is that the filling transition is due to an intrinsic instability in the configuration of the liquid on the walls of an empty pore.¹⁵ On the other hand, the transition that takes place as the chemical potential is lowered, $\sigma_i = 1 \rightarrow 0$, is due to an instability at the liquid/vapor interface between a filled pore and an empty neighboring pore.¹⁵

The model defined by the rules (a)–(g) is the capillary condensation model (CCM). It has no single pore hysteresis but rather asymmetry between pore filling and pore emptying due to the access condition for emptying. The access condition is a pore-pore interaction, thus the CCM is a model of an interacting (pore) system. The CCM is similar to the models of Mason¹² and Parlar and Yortsos¹³ which also eschew single pore hysteresis.

We complete this introduction to the CCM with a short glossary. The state of each pore is described by a spin σ_i that responds to an external field μ , an internal random field ϕ_i (or p_i), and an internal interaction field ν_i . The response of σ_i to the external field μ depends the relationship between the strength of μ and the strength of the internal fields. A chemical potential protocol is an external field protocol.

III. RESULTS

In Fig. 1 we show the result of carrying an $L/b = 256$ realization of the CCM through the chemical potential protocol shown in the inset (an illustration of the type of fluid configurations involved as the capillary condensation process proceeds is shown, for example, by McCall and Guyer¹⁶). In this figure we report the fraction of pores in the state $\sigma = 1$,

$$f = \frac{1}{N} \sum_{i=1}^N \sigma_i, \quad (3)$$

as a function of μ . The arrows on the figure indicate the direction of the evolution of μ . Let us look at a number of specific features.

(1) Because of the mapping of the set of ϕ_i onto $0 \leq p_i \leq 1$ the pore filling process is described by $f = \mu$.

(2) As the chemical potential is decreased from point 1 the evolution of f differs from its evolution as the chemical potential is decreased from point 2. The pores that empty as μ is decreased from point 1 are unable to empty when the same chemical potential change occurs as μ is decreased

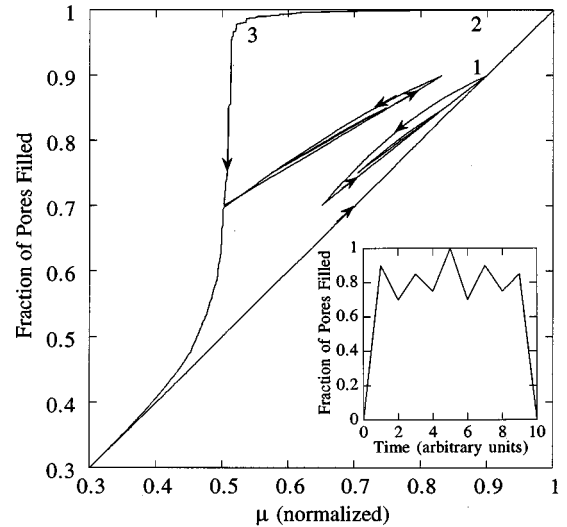


FIG. 1. Capillary condensation model. Fraction of filled pores versus scaled external chemical potential. The chemical potential protocol is shown in the inset. Arrows indicate the direction of chemical potential change.

from point 2. This feature is common in experimental isotherms.⁴ A simple Preisach model is inadequate to describe the system.

(3) The evolution of f near point 3, $p \approx p_c = 1/2$ as μ is decreased, is the invasion percolation process. In this process the vapor network gains access to the interior of the pore space from the perimeter. The vapor network is the incipient infinite cluster of percolation theory. Its geometry, size, etc., are governed by critical exponents from percolation theory. Thus

$$1 - f \approx |p - p_c|^\beta, \quad (4)$$

where $\beta = \nu(d - d_F)$. The region where f obeys this rule is hard to see in detail because it is rather narrow. For $d = 2$, $d_F \approx 1.9$, $\nu \approx 4/3$, and $\beta = 0.14$; the evolution of f from 1 to 0.5 occurs over $|p - p_c| \approx 0.008$ for an infinitely large system. In three dimensions, $d = 3$, $d_F \approx 2.5$, $\nu \approx 0.88$, and $\beta \approx 0.44$; the critical region is broader in μ in three dimensions than in two dimensions.

(4) Figure 1 exhibits hysteresis and discrete memory. The outside loop, $f = 0 \rightarrow 1 \rightarrow 0$, is simple percolation followed by invasion percolation. The interior loops involve the chemical potential protocol shown in the inset. All of the chemical potential cycles are hysteretic and display discrete memory.

IV. REMARKS

The capillary condensation process described by the rules in Sec. II has hysteresis with discrete memory. Hysteresis with discrete memory (H/DM) is seen in a wide variety of physical and model systems, e.g., in the equation of state of ferromagnets¹ and martensites,² in the elastic response of consolidated materials (rocks, soils),³ in the capillary condensation process,⁴ in the mechanical response of a frictional contact,⁵ and in the behavior of the disordered ϕ^4 chain.⁵ Models of H/DM are roughly of two kinds: (a) independent pore models like the Preisach model and (b) interacting pore

models like the random field Ising model (RFIM).

The Preisach model of H/DM has been in use for a long time in many disciplines.^{9,3,2,5} In a Preisach (noninteracting pore) description of the capillary condensation process the pores respond independently to the chemical potential protocol. A chemical potential pair (ϕ_i^F, ϕ_i^E) is associated with each pore. The transition $\sigma_i=0 \rightarrow 1$ occurs as μ passes ϕ_i^F going upward; the transition $\sigma_i=1 \rightarrow 0$ occurs as μ passes ϕ_i^E going downward. As noted in Sec. III, the Preisach model will give H/DM, but cannot produce the invasion (point 2, Fig. 1) versus no invasion (point 1, Fig. 1) results discussed in item (2). Interactions between pores are necessary to adequately describe the emptying process in capillary condensation.

Explanations of H/DM in terms of the RFIM are more recent. Sethna and co-workers^{14,17} have demonstrated and argued that the RFIM has H/DM. In the RFIM there is a magnetic field on each spin (pore), given as the sum of the external field H_0 (μ), a random internal field F_i (ϕ_i), and the interaction of the spin (pore) with its near neighbors. Thus

$$h_i = H_0 + F_i - J \sum_{j=1}^z \sigma_j \equiv H_0 + H_i. \quad (5)$$

The low temperature ($T=0$) evolution of this model depends on the sign of h_i . As H_0 is increased to above H_i , $h_i \rightarrow 0^+$, and $\sigma_i=0 \rightarrow 1$; as H_0 is decreased to below H_i , $h_i \rightarrow 0^-$, and $\sigma_i=1 \rightarrow 0$.

The CCM differs from the RFIM modestly but importantly. In CCM the transitions are asymmetric between increase and decrease of the external field, rules (f) and (g). In addition the fields that determine the transition as the external field is swept downward are not additive. In the CCM the transition is determined separately by the condition of ϕ_i and the access field ν_i in Eq. (2). For the transition to occur we need both μ to pass to below ϕ_i and $\nu_i < 0$. The condition $\nu_i < 0$ is a logical condition on the pore emptying process rather than an additive condition. In other words, ν is not multiplied by a parameter J [Eq. (5)] that can be made very small or very large. The internal fields ϕ_i and ν_i are additive in the RFIM and give rise to competition between the strength of the disorder, the width of $\tau(\phi)$, and the strength of the interaction J in determining the behavior of the system. The behavior of the CCM on decreasing the chemical potential is primarily determined by the logical condition $\nu < 0$ and secondarily by the relative strengths of μ and ϕ_i .

In mean field theory the CCM is described by (1) μ increasing, $f=p$ and (2) μ decreasing,

$$f = 1 - (1 - f^z)(1 - p) = R(f; p, z) = p + f^z(1 - p). \quad (6)$$

The second term in $R(f; p, z)$ is the product of the probability that a pore is open at p , $1-p$, and the probability that the access field is less than zero, $(1 - f^z)$. The invasion process occurs at

$$\left. \frac{\partial R}{\partial f} \right|_{f=1} = 1 \quad (7)$$

or $p = (z-1)/z$. $p \rightarrow 1$ as $z \rightarrow +\infty$ in qualitative agreement with known results. At $p < p_c$, $1 - f \propto |p_c - p|$, i.e., $\beta = 1$.

There are a number of physical realizations of the CCM and related models that are of considerable interest. We remark on three.

(1) Fluids in Nuclepore.⁴ The behavior of fluid configurations in porous media has elements of both the Preisach model and the CCM model. Nuclepore filters offer the possibility of tuning the interaction by adjusting the number of pores per unit area, and controlling the mix of Preisach/CCM in their behavior.

(2) Fluids in vycor.^{18,19} For example, the ⁴He fluid is a superfluid and supports the third sound mode. The propagation properties of this mode are a delicate probe of the structure of the fluid configurations in the pore space. Near invasion percolation the third sound mode probes the elasticity of the perimeter of the incipient infinite cluster. The proper description of wave propagation in this system raises matters of principle that have a counterpart in elastic wave propagation in consolidated materials. The understanding of these matters of principle, the formulation and solution to wave propagation in systems with hysteretic elasticity, is a subject of current interest.²⁰

(3) Self-organized criticality and avalanches. As the invasion percolation event unfolds the pore space is emptied in a series of avalanches. The spectra of avalanche sizes before and after percolation have power law dependences. The relevant exponents are a current subject of study.

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¹D. C. Jiles and D. L. Atherton, *J. Appl. Phys.* **55**, 2115 (1984).

²J. Ortin, *J. Appl. Phys.* **71**, 1454 (1991).

³D. J. Holcomb, *J. Geophys. Res.* **86**, 6235 (1981).

⁴M. P. Lilly, P. T. Finley, and R. B. Hallock, *Phys. Rev. Lett.* **71**, 4186 (1993).

⁵R. A. Guyer (private communication).

⁶F. Preisach, *Z. Phys.* **94**, 277 (1935).

⁷I. D. Mayergoyz, *J. Appl. Phys.* **57**, 3803 (1985).

⁸J. W. Macki, P. Nistri, and P. Zecca, *SIAM Rev.* **35**, 94 (1993).

⁹D. H. Everett, in *The Solid-Gas Interface, II*, edited by E. A. Flood (Marcel Dekker, New York, 1967).

¹⁰D. Wilkinson and J. Willemsen, *J. Phys. A* **16**, 3365 (1983).

¹¹D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, London, 1992).

¹²G. Mason, *J. Colloid Interface Sci.* **99**, 277 (1983); *Proc. R. Soc. London Ser. A* **415**, 453 (1988).

¹³M. Parlari and Y. C. Yortsos, *J. Colloid Interface Sci.* **124**, 162 (1988); **132**, 425 (1989).

- ¹⁴J. P. Sethna, K. Dahmen, S. Kartha, J. A. Krumhansl, B. W. Roberts, and J. D. Shore, *Phys. Rev. Lett.* **70**, 3347 (1993).
- ¹⁵S. M. Cohen, R. A. Guyer, and J. Machta, *Phys. Rev. B* **33**, 4664 (1986).
- ¹⁶K. R. McCall and R. A. Guyer, *Phys. Rev. B* **43**, 808 (1991).
- ¹⁷K. Dahmen, Ph.D. thesis, Cornell University, 1995.
- ¹⁸A. J. Brown, Ph.D. thesis, Bristol, 1963.
- ¹⁹J. H. Page, J. Liu, H. W. Deckman, and D. A. Weitz, *Phys. Rev. Lett.* **71**, 1216 (1993).
- ²⁰K. R. McCall and R. A. Guyer, *J. Geophys. Res.* **99**, 23 887 (1994).