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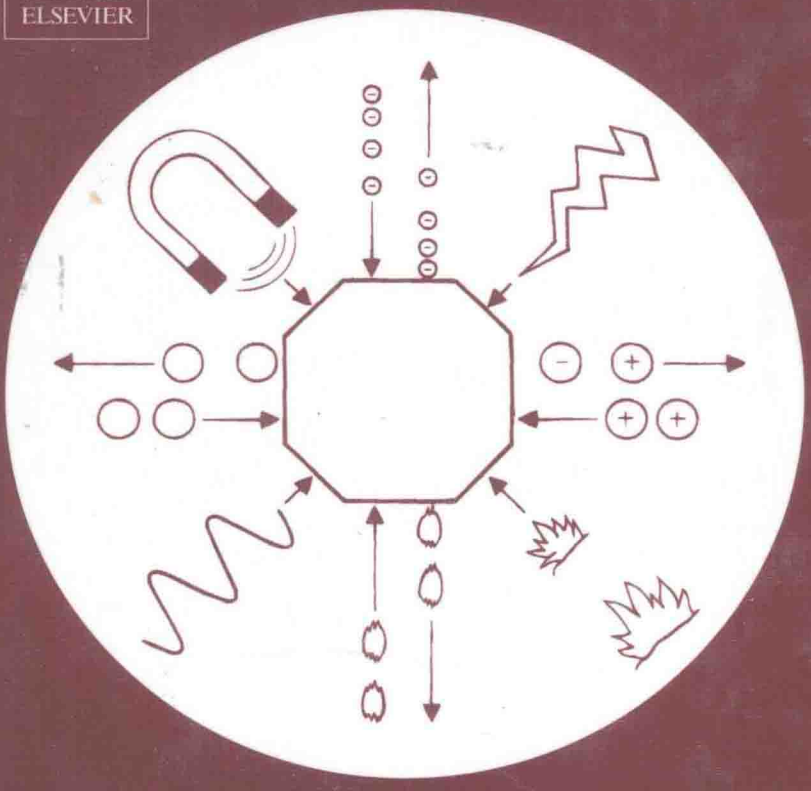

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CHARACTERIZATION OF POROUS SOLIDS VII

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(editors)

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CHARACTERIZATION OF POROUS SOLIDS VII

Proceedings of the 7th International Symposium on the Characterization of Porous Solids (COPS-VII), Aix-en-Provence, France, 26-28 May 2005

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Foreword

The The 7th International Symposium on the *Characterization of Porous Solids* (COPS-VII) was held in the Congress Centre in Aix-en-Provence between the 25th – 28th May 2005. This conference was the seventh in the series launched by the former IUPAC Commission of Colloid and Surface Chemistry and which began in 1987 in Bad Soden, Germany .

We welcomed around 230 guests from 27 countries. It is noteworthy that 31% of the participants were female and 12% of participants were from Industry. This industrial participation shows the interest of porous materials to processes. There were 36 oral presentations and 166 posters were given.

An intensive program over the three days was devoted to recent results of fundamental and applied research on the characterization of porous solids. Papers relating to characterization methods such as gas adsorption and liquid porosimetry, X-ray techniques and microscopic measurements as well as the corresponding molecular modelling methods were given. These characterization methods were shown to be applied to all types of porous solids such as clays, carbons, ordered mesoporous materials, porous glasses, oxides, zeolites and metal organic frameworks. A large part of this symposium was devoted to the use computational methods to characterise these porous solids.

I would like to express my thanks to the organising committee (J. Rouquerol, F. Rodriguez-Reinoso, N. A. Seaton) for their help in composing a wide spectrum of presentations for an outstanding program of scientific quality. Many thanks also go to the local organising committee and all the young volunteers who ensured the smooth running and friendly atmosphere so typical of this conference series.

Finally I would like to acknowledge the financial support of Micromerticis S.A., Quantchrome, Region Provence Alpes Côte d'Azur, Rubotherm GMBH, Thermoelectron and Université de Provence who enabled the reduced fees for 36 students.

It has been decided that COPS-VIII will be held in Edinburgh, United Kingdom.

P. L. Llewellyn *Marseille, France*

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Effect of pore morphology and topology on capillary condensation in nanopores: a theoretical and molecular simulation study

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1. ABSTRACT

We report a theoretical and simulation study of the temperature dependence of adsorption hysteresis for porous matrices having different morphologies and topologies. We used off-lattice Grand Canonical Monte Carlo (GCMC) simulations and two Density Functional Theories (DFT): we used the standard DFT in the non local approximation for cylindrical pores and the coarse-grained lattice DFT developed by Kierlik *et al.* [7] for disordered porous materials. We aim at gaining some insights on the concept of critical hysteresis temperature defined as the temperature at which the adsorption/desorption isotherm becomes reversible.

2. INTRODUCTION

Capillary condensation occurs when a fluid is confined within nanopores. It is analoguous to the usual gas-liquid transition but displaced towards lower pressure because of confinement. In fact, capillary condensation concerns pores large enough so that the transition can occur due to cooperative interactions between adsorbed molecules. In contrast, such a phenomenon is not expected in micropores of a few angstroms. The status of capillary condensation in nanoporous adsorbents as being or not a first order transition is still the subject of intense research. Theoretical works for slit pores have demonstrated the existence of a true first order transition with a so-called capillary critical point characterized by a critical temperature of the confined fluid T_{cc} that is lower that of the bulk T_c^{3D}. In a pioneering work on the criticality of fluids between plates [1,2], Fisher and Nakanishi showed that the critical behavior is affected by the finite thickness of the adsorbed film and its interaction with the wall. This scaling theory predicts that pore condensation and the related hysteresis loop disappear at a temperature, T_{cc}, that is below the bulk critical temperature, T_c^{3D}. The shift in critical temperature $\Delta T_{cc}=T_c^{3D}-T_{cc}$ is dictated by the ratio of the pore width D and the correlation length ξ_0 of the density fluctuations in the bulk fluid:

$$\frac{\Delta T_{cc}}{T_c^{3D}}=C\left[\frac{\xi_0}{D}\right]^{1/\nu} \qquad (1)$$

In the 3D-Ising model, $\nu = 0.63$ and ξ_0 is of the order of magnitude of the molecular diameter σ. C is a constant that takes the universal value of 1.658 for zero fluid/wall interactions or 3.432 for strong fluid/wall interactions. In the classical mean field van der Waals fluid theory, $\nu = 0.5$ and ξ_0 is again of the order of magnitude of σ. C takes the universal constant value of 1.645 for zero fluid/wall interactions, which is close to the value found in the Ising approach, or takes the value of 4.284 for strong fluid/wall interactions. Critical-point shifts in a slit-like geometry can be rationalized by the facts that the fluid is between a 3D and a 2D states and that T_c^{2D} is much smaller than T_c^{3D}. Evans *et al.* [3] used the Density Functional Theory (DFT) and derived another expression for the shift in the critical temperature for a fluid confined in small pores:

$$\frac{\Delta T_{cc}}{T_c^{3D}} \approx \frac{1}{\lambda D} \qquad (2)$$

where $1/\lambda$ is the range of the fluid-fluid interaction, which is equal to the adsorbate size in reference [4]. Equation (2) is compatible with the 2D-Ising fluid theory since ν equals 1.

An adsorption/desorption isotherm below T_{cc}, exhibits a hysteresis loop. In between condensation and evaporation metastable pressures, there is an equilibrium pressure for which both the gas and liquid phases coexist. In the case of cylindrical pores of any dimensions, there are theoretical arguments to indicate that no first order transition can exist because at the critical point, the correlation length can diverge only in the direction of the pore axis; a cylindrical pore can be considered as a one-dimensional system whatever its diameter. However, DFT [4], simulations [5] and experiments suggest that fluids in both confining geometries (slit and cylinders with size of several nm) behave similarly as far as condensation and evaporation are concerned; the hysteresis loop shrinks as temperature increases and eventually disappears. We note that in a van der Waals picture of gas-liquid transitions in such simple systems, the temperature of hysteresis disappearance is the capillary critical temperature, i.e., T_{cc}.

Over the last decade, significant theoretical advances have been achieved regarding the understanding of fluids confined in a disordered porous materials; it is now clear that fluids in a network of pores having topological and morphological disorders (such as Vycor or CPG) strongly affects capillary condensation as compared to that in independent pores of simple geometries [6]. The first effect is a flattening of the adsorption isotherm branch, which therefore does not exhibit any discontinuity as in a slit or a cylindrical pore. The desorption branch remains vertical and defines a hysteresis loop that shrinks and disappears with increasing temperature. In a random matrix, Kierlik *et al.* [7] used a coarse-grained lattice gas theory (see below) and showed that, for large values of the ratio of the surface-fluid to fluid-fluid energies (parameter y), capillary condensation cannot be a first order transition when averaging over matrix disorder. The disorder generates a complex free energy landscape, with a large number of local minima (i.e., metastable states), in which the system remains trapped without finding the true equilibrium state; capillary condensation is then described as an out-of-equilibrium phenomenon. Detcheverry *et al.* [8,9] used the same coarse-grained theory for fractal porous materials and found evidence for a first order capillary condensation that depends on the porosity; it is first order in aerogels with 98% porosity but no longer in aerogels with 87 % porosity. Woo and Monson [10] used again this on-lattice mean field theory for Vycor glasses (mean pore diameter 4-5 nm) and found evidence of a true first-order transition with a critical point at a temperature lower than T_{cc} (the shift of the real critical temperature compared to T_{cc} increases with the coupling parameter y). However, the mapping

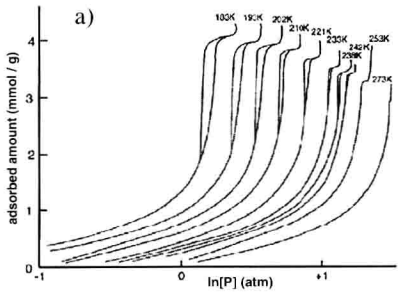

Fig. 1a. Xe Adsorption isotherms in Vycor at different temperatures. From Ref. [25].

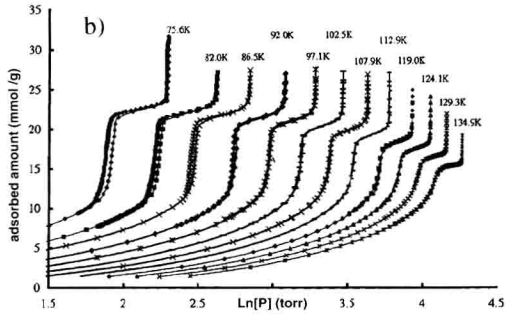

Fig. 1b. Temperature dependence of Ar adsorption isotherms in MCM-41 (D = 4.4 nm), T_{cc}= 102.5 K. adapted from Ref. [26].

of these on-lattice results on more realistic situations attainable with atomistic off-lattice techniques [11] remains difficult (in particular concerning the dependence of on-lattice results with the lattice spacing and the absolute value of y). We note that Monte Carlo simulations on a single (small) periodic Vycor also suggest the existence of a first order transition [12,13,14], when analyzing adsorption data for Ar and H_2O over a wide range of temperatures. However, such atomistic simulations do not consider any averaging over the matrix disorder. The extent of the pore topological disorder therefore seems to have some influence on the nature of capillary condensation. More recently, Coasne and Pellenq [15] showed the important effect on condensation and evaporation of extended morphological defects within a single cylindrical pore such as a constriction. Upon adsorption, the dense phase nucleates in the constrictions and subsequently propagates in the larger cavities (with a meniscus) until a gas bubble is formed and eventually collapses. Upon desorption, evaporation can follow either the so-called pore blocking mechanism (i.e., the larger pore region remains filled until the constricted region empties) or a cavitation process (i.e., the liquid in the largest pore regions undergoes a liquid-gas transition while the constricted regions remain filled), depending on the constriction size and the ratio of the fluid-fluid to fluid-wall energies [16]. These findings confirmed those obtained for constricted slit [17,18,19] and cylindrical [20] pores. Independent but constricted cylindrical pores give rise to adsorption/desorption isotherms, whose shape closely resembles that observed for connected porous networks, in agreement with the recent experiments by van der Voort *et al.* on plugged MCM-41 pores with silica clusters [21]. A constriction can therefore be viewed as a connection between two pores and a constricted single pore can be considered as the simplest model for connected porous materials. Up to now, we have only described results for infinite (periodic) systems, i.e. with pores that are not directly connected to the gas phase through the external surface of the material. If a simple cylindrical pore is connected to the external gas reservoir, then it was shown that desorption occurs at equilibrium [18]. A pore with a close end have a reversible adsorption isotherm with a sudden increase upon condensation (decrease upon evaporation) in the adsorbed amount at a pressure equal to the equilibrium pressure of the equivalent infinite pore (which corresponds to the desorption pressure of the open ended pore of the same diameter or width). Therefore, open ended pores or infinite pores of the same size will have the same hysteresis critical temperature. In disordered porous systems, the status of T_{cc} as being or not relevant to a true critical point is not clear as it seems to depend on the type and degree of disorder (random or fractal porous networks or correlated structures such as Vycor).

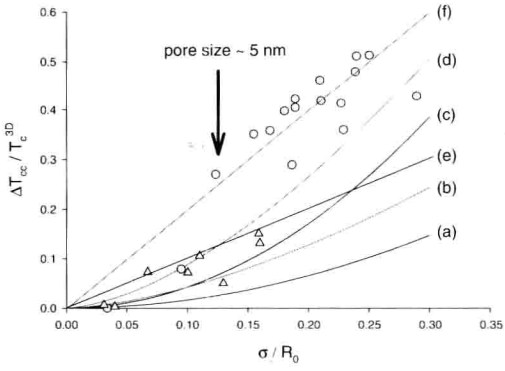

Fig. 2. Experimental hysteresis critical temperatures for various confined fluids. T_c^{3D} is the bulk critical temperature and $\Delta T_c=[T_c^{3D} - T_{cc}]$. Experimental data from [26,22,27,28]. (a) 3D-classical fluid theory with zero wall-fluid interaction, (b) 3D-Ising fluid theory with zero wall-fluid interaction, (c) 3D-classical fluid theory with strong wall-fluid interactions, (d) 3D-Ising fluid theory with zero wall-fluid interactions, (e) 2D-Ising fluid theory with $1/\lambda=\sigma$, (f) same as (e) with $1/\lambda=2\sigma$.

After these theoretical considerations, one should turn to experimental results. Materials made of unconnected pores are for instance MCM-41 [23] and porous silicon for instance [24]. A standard nanoporous disordered material (with connected pores, and a mean pore size ~ 5 nm) is Vycor glass. Experimental data of T_{cc} in these porous systems are rather scarce as it requires adsorption/desorption isotherms over a wide range of temperatures. This was done for Vycor by Burgess *et al.* in the case of Xe and CO_2 [25]. Very recently, Morishige *et al.* were able to measure a complete set of adsorption isotherms for several simple adsorbates such Ar, N_2, O_2, etc. in MCM-41 materials of several pore diameters [26]. Figure 1 presents experimental data for Xe in Vycor and Ar in MCM-41 (D = 4.4 nm). Gathering all available data together, one can plot the reduced shift of T_{cc} (with respect to the bulk fluid critical temperature) with the reduced pore dimension (with respect to the adsorbate diameter) as originally proposed by Thommes *et al.* [27] and Sing *et al.* [28] using experimental data of simple fluids in CPG and MCM-41 samples. This is presented in Figure 2 for a collection of fluids including Ar, Xe, N_2, O_2, SF_6, CO_2, C_2H_2 in various MCM-41 and Vycor. Clearly, none of the 3D (classical or Ising) theories is able to describe the data for MCM-41 with pore diameter smaller than 5 nm. Data for larger MCM-41 pores and disordered materials are reasonably well described using the 3D-Ising theory with strong wall-fluid interactions. To our knowledge, there is no available T_{cc} data for fluids confined in disordered porous materials with mean pore size smaller than 5 nm. Data for MCM-41 pores with diameter smaller than 5 nm are adequately described using the 2D-Ising fluid theory with $1/\lambda=2\sigma$. It seems that the mean pore size matters more than the degree of disorder as data for large MCM-41 mix with those for disordered systems.

In this work, we aim at gaining insights at a molecular level on the hysteretic behavior of adsorption/desorption isotherms of several fluids confined in a rather large collection of pore models that includes single pores of various geometries (cylinders, ellipsoids, constricted pores and Vycor).