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# Light scattering reveals the influence of temperature on collective effects during evaporation and condensation in a disordered porous material

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## Abstract

We combine high resolution isotherms measurements and light scattering technics to study over a broad temperature range collective effects during the condensation and evaporation of helium from Vycor, a prototypic disordered porous material. For evaporation, our results provide the first direct evidence for a crossover from a percolation collective mechanism at low temperature to a local cavitation mechanism at high temperature. No long range collective effects are detected during condensation. We compare these results to recent theoretical predictions emphasizing the specific role of disorder, and discuss their relevance for determining pores sizes distributions in disordered porous materials.

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Confining a fluid inside a wetting porous material results in an hysteresis between condensation and evaporation and a shift of the corresponding hysteresis loop below the bulk saturated vapor  $P_0$  [1]. The part played in this hysteresis by pore coupling and/or disorder has been studied by recent theoretical approaches [2–6] motivated both by the interest of this question in relation to statistical physics, and the need to understand how these effects affect the widely used Barrett-Joyner-Halenda (BJH) method of characterization of porous materials [7] which assumes independent pores. Up to now, these different approaches have been mostly probed by analyzing the shape of experimental adsorbed amount vs pressure isotherms. In this paper, we combine high resolution isotherms and light scattering measurements to directly investigate the collective effects involved in the condensation and evaporation processes in a disordered porous material, providing a new benchmark against which to test the applicability of the current theories of hysteresis to disordered porous materials.

In independent, cylindrical, pores, the situation assumed by the BJH method, evaporation occurs at equilibrium by recession of a nearly hemispheric meniscus from the pore ends, while condensation is delayed with respect to this equilibrium situation, occurring by a spinodal instability of the (metastable) adsorbed film [8]. BJH then use the Kelvin relation between the equilibrium pressure and the pore radius, modified to account for the presence of an adsorbed film [1], to determinate pore sizes distributions from the desorption isotherm. However, modulations of the pore radius along its length [9, 10], or connections between pores of different radii [2], are expected to modify this scheme, affecting the validity of the BJH approach. On adsorption, a pore can fill at equilibrium if one of its neighbors is already filled. Reversely, a pore will not empty at equilibrium if it has no free access to the vapor, i.e. if it is surrounded by smaller pores filled with liquid. Evaporation will be delayed until the neighbors empty (the so-called pore-blocking effect), or until thermally activated nucleation (cavitation) of a bubble occurs within the pore. These different evaporation processes have been evidenced in organized porous systems. The absence of pore-blocking in patterned silicon wafers has been interpreted in terms of cavitation [11, 12]. A transition from the pore-blocking to the cavitation regime when increasing the temperature has been reported in cage-like porous materials constituted of large cavities separated by small constrictions [13, 14].

In disordered porous materials, the conventional view is that, due to the pore-blocking

effect, combined with the random pores size distribution, evaporation occurs by a percolation process, at a pressure such that the pores which would be empty at equilibrium percolate to the sample surface [2]. While the characteristic sharp kink of the evaporation branch in such materials has been interpreted as a signature of such a process, it could also be due to elastic coupling between the pores [12] or cavitation [15]. Furthermore, a recently developed new theoretical approach, according to which hysteresis in disordered porous materials is controlled by disorder effects rather than by the pores size distribution [3, 4], also accounts for the main features of the hysteresis loop in Vycor, a prototypic disordered porous glass, including the kink [4] and slow relaxation dynamics [16], while showing *no* collective percolation effect during evaporation [17]. This makes clear that evaporation and condensation processes cannot be tested by the isotherm shape only, and that disordered materials might behave differently from ordered porous cage-like materials. Understanding the effects of pore coupling and disorder, a prerequisite for using the BJH equation to characterize such materials, thus requires a probe sensitive to collective effects.

Light scattering, which is sensitive to spatial correlations of the fluid distribution, is such a probe. However, for usual fluids, its use in transparent porous materials such as Vycor is hindered by very strong multiple scattering effects. Due to that, in the very few cases where it has been measured [18, 19], the light transmission along the steep part of the desorption branch is very small. Scattering measurements have been carried out in only one experiment, on hexane in Vycor, very close to the kink of the evaporation branch, where the transmission is close to unity [18]. The results exhibit an increase of the scattering at small angle characteristic of the fractal distribution of vapor expected for a percolation process. However, this result, only obtained at room temperature, far below the critical temperature  $T_c=570$  K, does not probe the sensitivity of the evaporation process to the temperature. In this paper, we report on a light scattering study of the mechanisms of condensation and evaporation of  $^4\text{He}$  in Vycor. The key advantage of using helium is its small scattering power [20], which avoids multiple scattering effects. This enables us to probe the correlations of the fluid distribution along the *whole* condensation and evaporation branches, *and* over a *broad* temperature range  $(0.57T_c - T_c)$ , shading a new light on the mechanisms of condensation and evaporation in disordered porous materials.

Our sample is a 4 mm thick, 14 mm diameter, disk of Vycor 7930 [33]. Standart analysis by nitrogen adsorption at 77 K yield a mean pore radius of about 4 nm with a standard

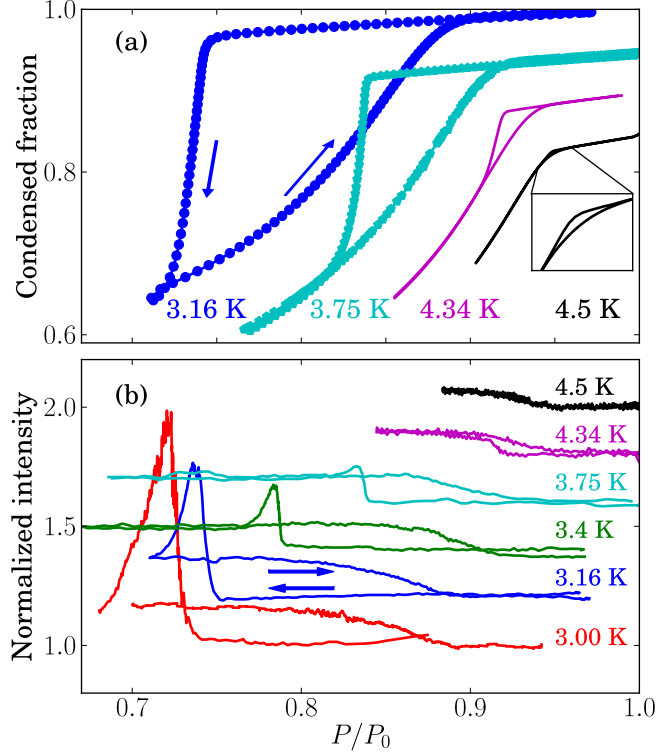


FIG. 1. Optical signature of a temperature dependent evaporation mechanism : (a) Adsorption and desorption isotherms for 3.16 K, 3.75 K, 4.34 K and 4.5 K. The condensed fraction in the sample is plotted *vs.* the reduced pressure  $P/P_0$ , where  $P_0$  is the saturated pressure at the considered temperature. Successive isotherms are vertically shifted by 0.05. (b) Corresponding scattered intensity at  $45^\circ$  for the same temperatures, plus 3 K and 3.4 K. The scattered intensity is normalized to its value at  $P_0$ . Successive curves are vertically shifted by 0.2.

deviation of 1 nm. Measurements are performed in an optical cryostat with 8 optical ports at  $45^\circ$  [22]. The disk is contained in an annular copper cell closed by two sapphire windows and regulated between 3 K and  $T_c \approx 5.2$  K. We measure with a high accuracy the fluid condensed fraction as a function of the applied pressure [23], when condensing or evaporating at a rate small enough (0.2 cc STP/min) to negligibly affect the shape of the isotherms. We illuminate the sample with a thin laser sheet at a wavelength of 632 nm under  $45^\circ$  incidence with respect to the common disk and windows axis, and image the illuminated slice with two CCD cameras facing the two windows (see figure in ref.[20]). From the grey level of these images, we obtain the light scattered by each illuminated point of the sample (at respective scattering angles of  $45^\circ$  and  $135^\circ$ , depending on the considered CCD).

Four characteristic isotherms are represented on figure 1(a). Below 4.34 K, the loop shape is nearly triangular in agreement with early measurements of Brewer and Champeney [24]. At larger temperatures, the loop shrinks, changing its shape to a more rounded one, and closes at a temperature  $T_{\text{ch}}^*$  between 4.6 and 4.65 K, 10% below  $T_c$ . We stress that this temperature evolution (steeper desorption branch at lower temperatures) is opposite to that previously reported for cage-like materials [13, 14], and for nitrogen on Vycor [25], and used as an argument in favor of a percolation to cavitation cross-over.

The optical signal measured along the isotherms is essentially homogeneous. Figure 1(b) shows the intensity scattered at  $45^\circ$  from the center of the Vycor sample. The behavior is strikingly different between condensation and evaporation. At all temperatures, the scattered intensity decreases during the condensation process, in quantitative agreement with the index matching effect resulting from filling the pores with liquid. In contrast, at the lowest temperature (3 K), the scattered signal exhibits a well marked peak along the steepest part of the desorption branch, exceeding the signal for the empty Vycor by a factor two. This difference between adsorption and desorption is consistent with previous transmission measurements performed on hexane [18] and argon [19] in Vycor. It shows that the spatial correlations of the helium distribution within Vycor extend on larger distances on evaporation than on condensation. Indeed, in the Rayleigh-Gans regime, the scattered intensity, for a given condensed fraction, increases with this correlation length, due to the coherent addition of scattered fields within the correlation volume. Moreover, on evaporation, because the scattering power of helium is small compared to that of silica, the two fold increase of intensity compared to the empty Vycor at the peak of the desorption signal implies that the corresponding correlation length of the helium is much larger than that for Vycor. This is confirmed by the angular dependence of the optical signal. For evaporation at 3 K, the ratio of the scattered intensities at  $45^\circ$  and  $135^\circ$  increases from 1 just after the kink in the isotherm to about 2 at the peak of the  $45^\circ$  intensity, before decreasing back to unity for smaller pressures. Such an anisotropy shows that the corresponding correlation length is of order a fraction of the optical wavelength, much larger than the typical correlation in Vycor (less than 20 nm [26]). We conclude that, at 3 K, pores empty by a collective mechanism, consistent with the occurrence of percolation. Unlike Page *et al* [18], we could not evidence the increase of the scattered signal at small angles, possibly due to the background intense forward scattering from the unperfectly polished surfaces of our sample. The evolution of

the optical signal up to  $T_{\text{ch}}^*$  unravels a change in the evaporation process. As the temperature increases up to 3.75 K, the optical signal peaks in the same range of condensed fractions (around 85%-90%) than at 3 K, but the peak height decreases. This is not due to the decrease of the optical contrast between liquid and vapor induced by the decrease of their density difference. At 3.75 K, the peak signal is only marginally larger than the empty Vycor signal, while the latter effect should lead to a decrease of the peak height of at most 20% as compared to 3 K. Finally, at 4.34 K and above, the signal is the same on condensation and evaporation, when plotted as a function of the condensed fraction rather than the pressure. This evolution shows that the length scale of the correlations induced by the evaporation process decreases with increasing temperature. This is consistent with the identity of the optical signal at  $45^\circ$  and  $135^\circ$  over the full pressure range for temperatures larger than 3.4 K included. This demonstrates that the evaporation mechanism changes with temperature, *included* in a temperature range where the isotherm triangular shape is retained.

We have compared this behavior to that expected for a simple model of cylindrical pores, incorporating both thermal activation and network effects. In a first step, we have generalized the calculation of Saam and Cole [8] to take into account thermally activated cavitation in a cylindrical pore of radius  $R$  [27]. This allows us to compute the equilibrium and cavitation pressures as a function of temperature and  $R$ , when barriers with energy of  $38 k_B T$  can be overcome [34]. These pressures become equal at a pore-dependent critical temperature  $T_{\text{ch}}(R)$ , above which condensation and evaporation in the considered pore occur reversibly at equilibrium. In a second step, we average the isotherms over a distribution of pores, assumed independent. Remarkably, we can qualitatively reproduce the observed temperature evolution of the isotherm shape assuming reasonable values for the pore size distribution and the van der Waals attraction to the wall [27]. This has two important consequences. First, it confirms that the shape of the sorption isotherms alone cannot be used to probe coupling effects in disordered porous materials. Second, in agreement with ref.[30] and in contrast to ref.[31], the closure of the hysteresis loop in Vycor can be accounted by cavitation, without implying a shift of the critical point due to confinement.

In a third step, we consider the effect of connections between pores. Fig. 2 shows the equilibrium and cavitation pressures as a function of temperature for different pore radii, using the Van der Waals potential determined as above. In Mason's percolation scenario [2], evaporation takes place at the equilibrium pressure for pores of radius  $R_p$  such that pores

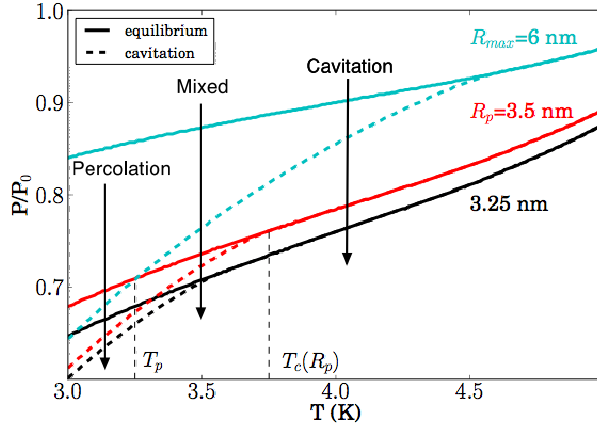


FIG. 2. Equilibrium and cavitation pressures versus temperature for cylindrical pores of radii 3.25, 3.5, 6 nm, computed for an energy barrier for activation of  $38 k_B T$ , and a Van der Waals interaction potential of helium at distance  $z$  from a half-space filled with silica  $U(z) = 1200 K \text{ \AA}^3/z^3$ . Vertical dashed lines indicate the upper limit  $T_p$  of pure percolation, and the lower limit  $T_c(R_p)$  of pure cavitation, for  $R_p=3.5$  nm (see text).

of radius  $R \geq R_p$  form a percolating network. This allows us to define three regimes of evaporation. Pure percolation is expected if no pore has yet cavitated at this pressure. This occurs below the temperature  $T_p$  such that the cavitation pressure of the largest pores (of radius  $R_{\max}$ ),  $P_{\text{cav}}(R_{\max}, T_p)$  equals the equilibrium pressure for pores of radius  $R_p$   $P_{\text{eq}}(R_p, T_p)$ . Reversely, percolation will not take place if all pores subject to hysteresis are already empty at the pressure where it would take place. This corresponds to temperatures larger than  $T_{\text{ch}}(R_p)$ . In the intermediate temperature range, pores of radius larger than  $R_{\text{cav}}(T)$  such that  $P_{\text{cav}}(R_{\text{cav}}, T) = P_{\text{eq}}(R_p, T)$  will evaporate before percolation would set in. In this case, we expect the percolation process to start from the empty large pores rather than from the Vycor surfaces, decreasing the correlation length of the vapor distribution, hence the optical signal.

In order to directly check this idea, we have studied evaporation at 3 K starting from an incompletely filled initial state. If pores mainly fill following their size ordering, as in the independent pores model, this should simulate the effect of evaporating from cavitated pores. As shown by figure 3, an hysteresis loop opens only when starting evaporation from a filled fraction larger than 80%. Correspondingly, an optical signal develops on evaporation and peaks at about the same pressure as in the fully filled case. Its amplitude increases with the



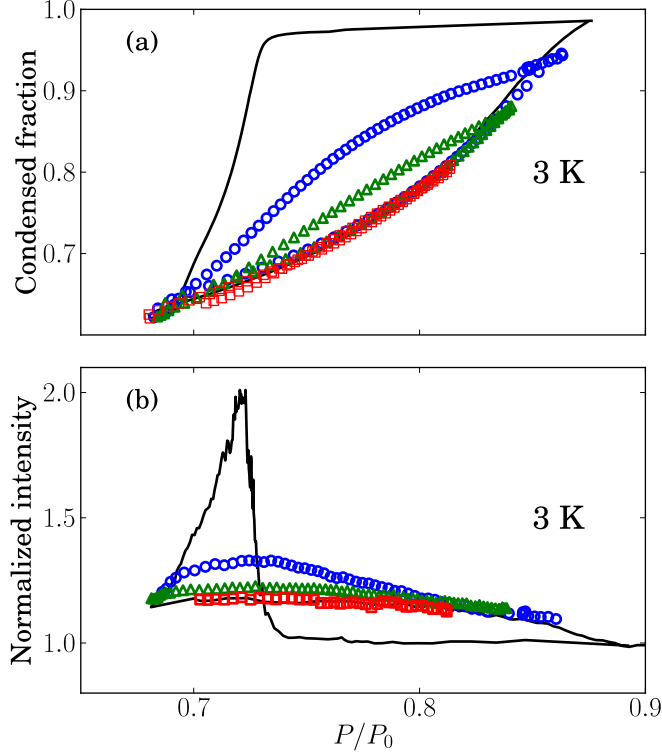


FIG. 3. Correlations during evaporation depend on the initial filling state : (a) Desorption scanning curves at 3 K. The difference between the complete adsorption isotherm (black line) and the adsorption scanning curves (open symbols) is due to a difference in flow rate. (b) Normalized intensity along the full loop and the different desorption scanning curves.

reversal fraction, but remains much smaller than for the fully filled case even for a reversal fraction of 95%. Hence, even a small fraction of initially empty pores strongly decreases the optical signal. The intermediate regime in fig. 2 should then be identified to the temperature range where the optical signal disappears. Accordingly, our optical results (marked decrease of the scattered intensity beyond 3.16 K, disappearance of the signal around 3.75 K) are consistent with the mixed cavitation/percolation scenario if we assume  $R_p \approx 3.5$  nm. This value is smaller than the average pore size of 4 nm deduced from the position and shape of the desorption isotherms in fig. 1 using the parameters of fig. 2 [27]. Percolation thus seems to require more than 50% of the pores to be empty, rather than  $\simeq 40\%$  in a random model of 3D percolation with coordinance 4. This might result from correlations in the distribution of pores.

In summary, our optical measurements provide the first direct demonstration that evap-

oration in a disordered porous material evolves from a collective process at low temperature to a more local process as the closure temperature of the hysteresis loop is approached. The overall behavior is consistent with a percolation to cavitation crossover. Simultaneously, the desorption branch of the isotherms gets less steep. We stress that this temperature dependence is *opposite* to that reported in ordered porous materials, and argued to be an evidence for a *similar* crossover, showing that the isotherms shape does not unambiguously probe this crossover. The measurement of long range correlations during evaporation seem to contradict the prediction of the disorder-based approach that cavitation is the dominant evaporation mechanism in Vycor [17]. This suggests that the disorder-based approach may not grasp all the physics of the evaporation in disordered porous materials. However, a definite conclusion would need a direct calculation (similar to that performed for silica aerogels [32]) of the light scattering within the latter approach, and to vary the system parameters used in the simulations.

The collective behavior of the evaporation process implies that pore distributions cannot be inferred from the desorption isotherm within the BJH model of independent pores. Mason [2] has proposed an alternative, based on the analysis of desorption scanning curves. Our results show that his method can be valid only far enough below  $T_c$  for cavitation to be negligible. On the other hand, the lack of optical signal during condensation shows that the effect of pore coupling is more limited than during evaporation. Although activated condensation (or spinodal instability) in a pore may trigger condensation at the equilibrium pressure in a neighboring pore of smaller radius, this coupling does not appear to propagate over large distances. We are currently extending our simple model above to incorporate in a realistic way the effect of coupling between pores. If such an extension does reproduce the observed behavior, it could be used to evaluate which fraction of pores fill at equilibrium, due to the coupling between pores. If this fraction is large enough, the BJH method could possibly be used along the adsorption isotherm to yield an approximately correct pore size distribution.

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