Light scattering study of collective effects during evaporation and condensation in a disordered porous material

F. Bonnet, M. Melich, L. Puech† and P. E. Wolf

Institut Néel, CNRS/UJF - BP 166, 38042 Grenoble-Cedex 9, France, EU

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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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Introduction. – Confining a fluid inside a wetting porous material results in a 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, connections between pores of different radii [2], or modulations of the pore radius along its length [9,10], 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. In all cases, the pore size distribution deduced from the BJH approach would be wrong.

In the past decade, progresses in chemical synthesis have allowed to produce ordered porous materials with controlled geometry, and to evidence these different mechanisms. 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 such materials, it has been shown that the cavity size is much better predicted from the adsorption isotherm,
assuming that condensation takes place close to the spinodal pressure, than from the desorption isotherm following the BJH approach [15].

The situation in disordered porous materials is presently unsettled. In the conventional view, 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. In this scenario, Mason has proposed a method to extract the pores size distribution by analyzing a series of desorption scanning curves, i.e. desorption isotherms starting from different points on the adsorption isotherm [2]. The characteristic sharp kink of the evaporation branch in disordered porous materials such as Vycor, a prototypic disordered porous glass, has been interpreted as a signature of the validity of the percolation scenario. However, based on studies on organized materials, some authors have suggested that the kink could also result from elastic coupling between the pores [12] or cavitation [16]. 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, including the kink [4] and slow relaxation dynamics [17], while showing no collective percolation effect during evaporation [18]. Hence, disordered materials might behave differently from ordered porous cage-like materials. Understanding the effects of pore coupling and disorder, a prerequisite for using characterizing 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 [19,20], 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 [19]. 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 $T_\text{c} = 570$ 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 $^4$He in Vycor. The key advantage of using helium is its small scattering power [21], 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 ($0.57T_\text{c} - T_\text{c}$), shedding a new light on the mechanisms of condensation and evaporation in disordered porous materials.

Experimental. – Our sample is a 4 mm thick, 14 mm diameter, disk of Vycor 7930. Standard analysis by nitrogen adsorption at 77 K using a commercial apparatus (Micromeritics ASAP 2010) yields a mean pore radius of 2.8 nm (respectively, 3.5 nm) if the pores are assumed to empty (respectively, fill) at equilibrium and the BJH approach is applied to the desorption (respectively, adsorption) isotherm. This illustrates the sensitivity of the pores size determination to the assumed mechanisms for condensation or evaporation. Our own measurements are performed in an optical cryostat with 8 optical ports at 45° [22]. The disk is contained in an annular copper cell closed by two sapphire windows and regulated between 3 K and $T_\text{c} \approx 5.2$ 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° incidence with respect to the common disk and windows axis, and image the illuminated slice with two CCD cameras facing the two windows (fig. 1). 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° and 135° (depending on the considered CCD).

Results. – Four characteristic isotherms are represented in fig. 2(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 and closes at a temperature $T_\text{ch}$, between 4.6 and 4.65 K, 10% below $T_\text{c}$. The accuracy of our isotherms measurements makes clear that the loop shape evolves from a triangular shape to a more rounded one as $T_\text{ch}$ is approached, i.e. the desorption branch becomes less steep as temperature increases. Noticeably, this evolution 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.

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Fig. 1: (Colour on-line) (a) Top view of the optical set-up, showing the Vycor disk between two flat windows, and (b) picture taken at 45°. The whiter band is the region illuminated by the light sheet. The scattered intensity is measured by the average grey level inside the central box.

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Advanced Glass and Ceramics, Holden, MA, USA.
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Fig. 2: (Colour on-line) 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.

We have compared the measured temperature evolution of the hysteresis loop to that expected for a distribution of independent cylindrical pores, assuming that pores can only empty by cavitation (rather than from the pore ends). To this aim, we have generalized the calculation of Saam and Cole [8] to take into account thermally activated cavitation or condensation in a single cylindrical pore of radius $R$ [26]. This allows us to compute the condensation and cavitation pressures as a function of temperature and $R$, when barriers of energy $E_b = 38 k_B T$ can be overcome$^2$. Both pressures become equal to the (R-dependent) equilibrium pressure at a pore-dependent critical temperature $T_{ch}(R)$, above which condensation and evaporation in the considered pore occur reversibly at equilibrium. In a second step, in a similar way to Saam and Cole [8], we average the isotherms over a Gaussian distribution of pores radii, assuming all pores to have the same volume (i.e. larger pores to have smaller lengths).

$^2$This is a typical value for cavitation in a single pore on a time scale of several hundreds of seconds: see, e.g., [14,27].

Fig. 3: (Colour on-line) Theoretical hysteresis loops for an assembly of independent pores when evaporation takes place by cavitation (see text). The temperatures correspond to those in fig. 2(a) and the curves are vertically shifted by 0.05 as in this figure.

Figure 3 shows that this simple model qualitatively reproduces the observed temperature evolution of the isotherm shape assuming reasonable values for the pore radius distribution (average radius of 4 nm with a standard deviation of 20%) and the same van der Waals attraction to the wall than taken by Saam and Cole (interaction potential of helium at distance $z$ from a half-space filled with silica $U(z) = 1200 K A^3/z^3$, from Sabisky and Anderson [28]). The fact that this model accounts for the closure of the hysteresis loop at $T_{ch}$ is evidence that evaporation takes place by cavitation close to $T_{ch}$. This conclusion is in agreement with ref. [29] and contrasts to ref. [30], which interprets the difference between $T_{ch}$ and $T_c$ as due to a shift of the critical point by confinement. Quantitatively, however, there are some differences. The experimental desorption curves are steeper than predicted, the pressure at the kink (or elbow) of these curves is somewhat larger than predicted, and their vertical spans smaller. Although these differences could result from the coupling between pores, they depend on the precise choice of physical parameters. This makes difficult to unambiguously probe coupling effects in disordered porous materials using the shape of the hysteresis loop only.

In contrast, light scattering clearly reveals that collective effects do exist on desorption, and depend on temperature. Figure 2(b) shows the intensity scattered at $45^\circ$ from the center of the Vycor sample (the optical signal measured along the isotherms is essentially homogeneous). The behavior is strikingly different between condensation and evaporation. At all temperatures, the scattered intensity decreases during the condensation process. The order of magnitude and the temperature dependence of the effect are consistent with the index matching resulting from filling the pores with liquid, the intensity change between empty and filled being of the order of the relative
change of $(K_{\text{Si}} - K_{\text{He}})^2$ between liquid and vapour helium, where $K = (\epsilon - 1)/(\epsilon + 2)$ and $\epsilon$ is the dielectric constant of silica (1.56) or helium, respectively. 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 condensation and evaporation is consistent with previous transmission measurements performed on hexane [19] and argon [20] in Vycor. It shows that the spatial correlations of the helium distribution within Vycor extend on larger distances in the latter case. Moreover, because the scattering power of helium is small compared to that of silica, the two-fold increase of intensity at the peak of the desorption signal, as compared to the empty Vycor, 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° and 135° increases from 1 just after the kink in the isotherm to about 2 at the peak of the 45° 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 [31]). We conclude that, at 3 K, pores empty by a collective mechanism. Unlike Page et al. [19], we could not detect the specific signature of percolation, that is the strong scattering at small angle at the kink of the desorption isotherm, when vapour is distributed on a percolation cluster. This is likely the drawback of the small scattering power of helium compared to hexane. Page et al.’s observation was performed for a transmission close to unity. Translated to our case, the corresponding scattered signal would be very small and could be hidden by the strong forward scattering from the unperfectly polished surfaces of our Vycor sample.

In our case, a percolation mechanism at 3 K is further supported by the behaviour of the optical signal during evaporation, when starting from an incompletely filled initial state. As shown by fig. 4, an hysteresis loop opens only when the initial fraction is larger than 80%. The larger the condensed fraction at the reversal point, the more open the loop. The partial desorption isotherm only joins the desorption branch of the full loop at its lower closure point. Both facts are in agreement with previous observations on Vycor [2], and with the behaviour of scanning curves predicted for correlated pores within the density functional theory [32]. 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 initial fraction, but remains much smaller than for the fully filled case even for a fraction of 95%. This strong sensitivity of the optical signal to a small fraction of initially empty pores is consistent with a percolation scenario. Indeed, if some pores are initially empty, evaporation will start when the potentially emptied pores at equilibrium percolate to the empty pores, rather than to the external surfaces of vapor. This should reduce the correlation length of the vapor distribution, hence the optical signal.

Above 3 K, fig. 2(b) shows that the optical signal decreases as 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 with temperature. 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 marginaly 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

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3In the relevant regime where the helium correlation length is smaller than the optical wavelength, the scattered fields within a correlation volume coherently add, so that a larger scattered intensity at a given condensed fraction means a larger correlation length.
The optical signal decreases with increasing temperature. This is consistent with the identity of the optical signal at 45° and 135° over the full pressure range for temperatures larger than 3.4 K included. Thus, our optical observations unravel a change of the evaporation mechanism with temperature, even though the triangular shape of the isotherm is initially retained.

We now show that this evolution is consistent with a crossover from percolation to cavitation. To this aim, we plot in fig. 5 the theoretical equilibrium and cavitation pressures as a function of temperature for different pore radii, computed within the model discussed above, using the the same Van der Waals potential as in fig. 3. In Mason’s percolation scenario [2], evaporation takes place at the equilibrium pressure for pores of radius \( R_p \), such that pores of radius \( R \geq R_p \) form a percolating network. This allows to define three regimes of evaporation. Pure percolation is expected at the percolation threshold 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 \((R_{\text{max}})\), \( P_{\text{cav}}(R_{\text{max}}, T_p) \) 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 occur. 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 from the surfaces sets in. In this case, we expect evaporation to occur by percolation from these empty pores, just as at 3 K, when starting from a not fully filled sample. As in fig. 4, this will decrease the optical signal. Hence, in a first approximation, the intermediate regime in fig. 5 should be identified to the temperature range where

\[ T_{\text{p}} < T < T_{\text{ch}}(R_p) \]

Conclusions. – In summary, our optical measurements provide the first direct demonstration that evaporation 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 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 [18]. This suggests that, although it properly accounts for the observed shape of scanning curves [32], 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 [33]) of the light scattering within the latter approach. Also, because the predictions for the disorder-based approach depend on the model parameters used in the simulations, these parameters should be varied with respect to those used in ref. [18].

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. Furthermore, our results show that the alternative presented by Mason [2], based on the analysis of desorption scanning curves, can only be valid far enough below \( T_c \) for cavitation to be negligible. The upper temperature of validity of Mason’s method, as compared to \( T_c \), will depend on the details of the considered

\[ T_{\text{ch}}(R_p) \]

In principle, above \( T_{\text{ch}}(R_p) \), pore coupling might give local correlations between empty pores, and a corresponding optical signal. Reversely, the optical signal might become too small to be measured even below \( T_{\text{ch}}(R_p) \). Furthermore, below \( T_p \), cavitation below the percolation pressure might already reduce the peak amplitude of the optical signal. We suspect that these effects have a modest impact at the level of the present discussion.
system (nature of the fluid, average pore size, attractive potential), so that no simple rule can be given. 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 the simple model discussed in this paper to incorporate in a realistic way the effect of coupling between pores. We plan to use this extension to understand the absence of an optical signal, then to evaluate which fraction of pores fill at equilibrium, due to the coupling between pores. If this fraction is large enough in some temperature range, the BJH method applied to the adsorption isotherm should yield an approximately correct pore size distribution. In the opposite case where pores would mainly fill independently, our model could be used to evaluate below which temperature thermal activation is small enough for the pores to fill at their spinodal pressure, as assumed in the method proposed in ref. [15].

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