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## Appearance of critical fluctuations in a binary fluid mixture confined in Vycor glass

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**Abstract.** We report here some of the results obtained through a small-angle neutron scattering experiment performed on a binary mixture absorbed inside Vycor porous glass. The aim of the experiment was to study the way the critical behaviour is modified when the mixture is spatially constrained to the random pore network of almost regular size (75 Å) characterizing the Vycor. The presence of concentration fluctuations inside the pores, the extent of which comes to exceed the mean pore size and increases more and more even below the bulk critical temperature, is observed.

The confinement of a fluid in porous media can lead to a strong change of its static and dynamic bulk properties. The way this alteration occurs generally depends on many parameters like the porous material topology and the characteristics of the interaction between the fluid and host matrix, for instance. Among the many related theoretical and experimental studies, the investigation of critical phenomena has been a topic of particularly increasing interest [1]. When the fluid is absorbed in a confining medium, a competition between effects due to the confinement, the preferential adsorption between one of the two phases and the host, the random nature of the pore network and that of its connectivity are expected, the relative importance of which varies according to the particular system under consideration. For highly porous materials such as gels, some experimental findings suggest that the predictions of the random-field Ising model (RFIM) could apply [2] for confined fluids [3]. This picture neglects the effect of confinement and represents the quenched random disorder introduced from the host as a source of the random field. When a mixture at critical concentration is absorbed in a porous medium, a transition from a bulk-like Ornstein–Zernike (OZ) behaviour, describing concentration fluctuations of correlation length  $\xi$ , to a combination of the OZ term with a Lorentzian squared (LSQ) one is predicted to occur close to the critical bulk temperature  $T_{bc}$ ; the result is

$$I(Q) = \frac{I_{OZ}}{1 + Q^2 \xi_{OZ}^2} + \frac{I_{LSQ}}{(1 + Q^2 \xi_{LSQ}^2)^2} \quad (1)$$

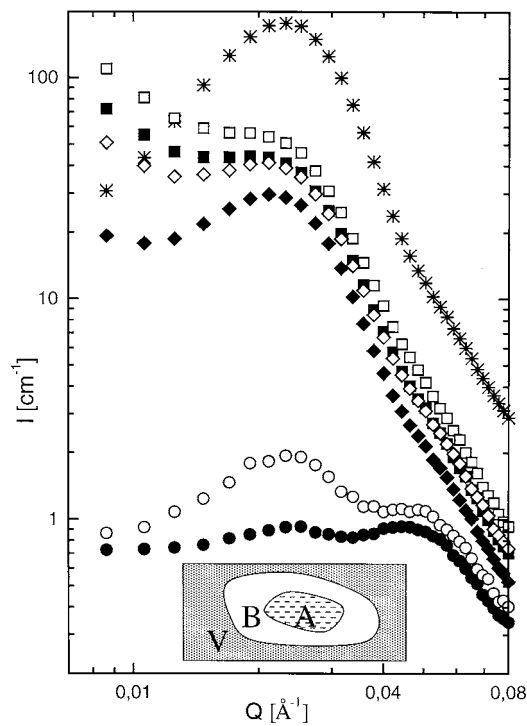
where  $Q$  is the momentum exchanged by the scattered radiation,  $I_{OZ}$  and  $I_{LSQ}$  are two intensities not depending on  $Q$ , and  $\xi_{OZ} = \xi_{LSQ}$ . A first small-angle neutron scattering experiment (SANS) [4] on water + lutidine at nearly critical concentration absorbed in Vycor glass has supported the validity of this first model; a complete-to-partial-wetting transition

was observed before the strongly history-dependent regime of frozen-domain states predicted from the RFIM was entered. Vycor is a rigid lightly porous ( $\approx 28\%$ ) silica glass obtained by spinodal decomposition and characterized from a highly interconnected random pore network, with a peaked pore size distribution centred at a value of the mean internal pore diameter given by  $\phi_v \approx 75 \text{ \AA}$  [5]. Due to the smallness of the pore sizes, it has been supposed that the RFIM could fail because confinement effects are expected to dictate the behaviour of the confined fluid; with these hypotheses, the single-pore model has been introduced [6]. According to this model, the porous matrix can be considered as an assembly of single cylindrical pores, the random nature of the network and its interconnectivity being negligible. The predictions are that  $\xi$  cannot exceed  $\phi_v$ , and that macroscopic phase separation cannot take place on the typical experimental timescales because of the presence of long relaxation times. A second SANS experiment [7] on the same system has supported this alternative interpretation, and the experimental data were again analysed according to (1) with  $\xi_{LSQ} \neq \xi_{OZ}$ . A result common to the two experiments was that only values of  $\xi$  well below the typical pore sizes were detected, maybe because of the preferential attraction between Vycor and lutidine that moved the concentration of the free fluid inside the pores away from criticality, as stated in [7].

In this paper we want to discuss some aspects of a recent SANS experiment [8] performed at the small-angle neutron scattering diffractometer PAXE of the Laboratoire Léon Brillouin (Saclay, France). We have measured the intensity scattered from the mixture  $n\text{-C}_6\text{H}_{14} + n\text{-C}_8\text{F}_{18}$  (hex + PFO) confined in Vycor glass. As these two fluids have similar attraction to the silica, we anticipated that the concentration shift in the pore could be reduced, and the onset of critical fluctuations enhanced. The thermodynamic region investigated was close to the bulk critical one that occurs at the critical concentration  $x_{PFO} \approx 0.35$ . This mixture presents a normal phase diagram; that is, at a temperature  $T > T_{bc} \approx 38 \text{ }^\circ\text{C}$  the system is in the homogeneous region. The SANS technique is well suited for the study of these phenomena, as it can probe concentration fluctuations in the range 10–1000  $\text{\AA}$ , and their relation to  $\phi_v$ . The intensity scattered from the two-species system A + B, as measured by a SANS experiment, is given by  $I_{AB}(Q) \propto K_{BA}^2 S(Q)$ , where  $K_{BA} = \rho_B - \rho_A$  is the contrast,  $\rho$  the neutron scattering length density, and  $S(Q)$  the structure factor. We have investigated three samples composed of  $\text{C}_8\text{F}_{18}$ ,  $\text{C}_6\text{H}_{14}$ , and  $\text{C}_6\text{D}_{14}$  with the same critical concentration  $x_{PFO}$ , whereas the concentration of  $\text{C}_6\text{D}_{14}$  was varied. As the scattering length density of hexane strongly varies with the deuterium content, we could then study the confined fluid behaviour for different values of its contrast with the Vycor. The thermodynamic characteristics of the three samples investigated are reported in detail in [8]; it is worth mentioning the influence of the deuteration on  $T_{bc}$ , that changes by roughly 3% passing from the sample that is completely hydrogenated (#H) to the one that is completely deuterated (#D). The contrast of Vycor always decreased in the presence of this mixture, but this effect was not particularly relevant for these two samples. Contrastingly, the third sample (#HD) was prepared with an intermediate degree of deuteration in such a way that the contrast with the glass was almost perfectly matched. The imbibing of the three mixtures was done inside the bulk single phase, at  $T \approx 60 \text{ }^\circ\text{C}$ . A few phenomena such as hysteresis, irreversibility, metastability, and slow relaxation may lead to substantial complications in such experiments, and add to the critical slowing down characterizing the phase separation. To study the influence of such effects, after the imbibing, #HD was left for two months at  $T \approx 0 \text{ }^\circ\text{C}$ . When the experiment was performed, its temperature was raised and its scattered intensity was measured together with those for the other two samples, without observing any time dependence of the signal. On the other hand, #H and #D showed a slow exponential relaxation to equilibrium, similar to what occurs for the relaxation of concentration fluctuations in a bulk mixture. A characteristic time  $\sim 100$  hours at  $T \approx 55 \text{ }^\circ\text{C}$  was measured, that became roughly halved at  $T \approx 50 \text{ }^\circ\text{C}$ ; at these temperatures equilibrium was not reached. The subsequent step

at  $T \approx 44.5$  °C allowed equilibrium to be reached within a few hours. The following four experimental temperatures, down to  $T \approx 15.5$  °C, confirmed the progressive decrease of the relaxation times, allowing us to obtain five thermodynamic states at equilibrium.

The intensity scattered from the empty Vycor,  $S_1(Q)$ , is reported in figure 1 together with the analogous quantities relating to the three samples at the highest and lowest temperature.  $S_1(Q)$  is mainly characterized by the known huge and broad peak typical of spinodal decomposition. This peak, centred at  $Q_{max} \approx 0.023$  Å<sup>-1</sup>, reflects the existence of a characteristic length  $\phi_v$ . At intermediate and high  $Q$  the intensities scattered from #H and #D are not apparently very different from  $S_1(Q)$ , apart from differences in the level of the signal due to the different contrasts. However, at low  $Q$ , we observe a sharp increase of the signal, increasing on lowering  $T$ . This behaviour could represent the manifestation of the occurrence of critical fluctuations, as discussed later. At  $Q \approx 0.05$  Å<sup>-1</sup> a second peak appears, more enhanced for #HD because of its low contrast. It is possible to associate this second peak, already seen in [4, 7], with the presence of a skin layer coating the pore walls and richer in one of the two fluids, say B (see the inset in figure 1). As experimentally demonstrated in [7], the presence of this layer introduces a second characteristic length in the system and, consequently, a new peak in  $S(Q)$ . No particular features at low  $Q$  characterize #HD, suggesting that, because of its irreversible history, it was already phase separated. It is possible to suppose that the layer and core structure depicted in figure 1 represent an ideal



**Figure 1.** A logarithmic plot of the intensity scattered from the dry Vycor (stars) and from the samples at the lowest (open symbols) and highest (full symbols) temperature. From the bottom: #HD (circles), #H (diamonds), and #D (squares). In the inset at the bottom a pore section with a layer richer in fluid B and a core part richer in fluid A is depicted; V stands for the Vycor. Such structure would give rise to a double peak similar to the one observed in the experimental data.

situation characterizing many pores but not all of them. In other pores, mainly the small ones, and in proximity to the many necks and corners existing in this porous medium, the formation of bubbles and domains richer in only one liquid probably takes place, thus giving a contribution to the signal mainly in correspondence to the first peak. Therefore, the tortuous and narrow nature of the host prevented the mixture from remixing, an operation difficult to achieve also in the bulk case while hardly stirring the sample. In the case of #H and #D, as the second peak was present, the analysis needed the inclusion of a model to describe this double structure. In [8] it was shown that a suitable function is given by

$$[K_{BV}\sqrt{S_1(Q)} - K_{BA}\sqrt{S_2(Q)}]^2 \quad (2)$$

Here  $K_{BV}$  ( $K_{BA}$ ) represents the contrast between the layer and the glass (core), and  $S_2(Q)$  is a second structure factor originating from the new quasiperiodic structure introduced from the layer, therefore with a peak at higher  $Q^\dagger$ . As Vycor is obtained by spinodal decomposition,  $S_2(Q)$  can be related to a different stage of the spinodal decomposition process forming the Vycor. A dynamical scaling law proportional to  $f(Q/Q_{max})Q_{max}^{-3}$ , where  $f$  is a universal function, can then be applied [8, 9]. In this way  $S_2(Q)$  was determined directly from the measured  $S_1(Q)$ , the former being lower than the latter because of the presence of the  $Q_{max}^{-3}$ -term.

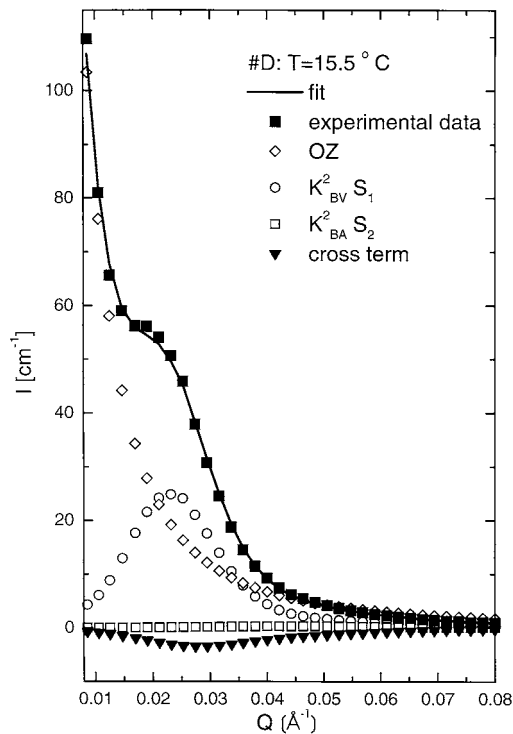
A fair agreement with the experimental results was obtained by fitting to the data the function

$$I(Q) = \frac{I_{OZ}}{1 + Q^2\xi^2} + [K_{BV}\sqrt{S_1(Q)} - K_{BA}\sqrt{S_2(Q)}]^2 \quad (3)$$

where the OZ term has been added to equation (2) to describe the experimental low- $Q$  behaviour, and  $I_{OZ}$ ,  $\xi$ ,  $K_{BA}$ , and  $K_{BV}$  are the parameters of the fitting function; in figure 2 an example of the fit result is shown. A second fit was performed adding also a LSQ term, but there was no evidence of any significant difference in the results. In figure 2 the contributions arising from the various terms of the fit are also displayed, to clarify their relative weight. The OZ term provides a large contribute to the total signal, implying the presence of concentration fluctuations of rather extended lengths. The component related to the B-Vycor interface,  $K_{BV}^2 S_1(Q)$ , is also rather large because of the low contrast. The less significant contribution comes from the contrast between the two fluid phases,  $K_{BA}^2 S_2(Q)$ , meaning that the difference in concentration between the layer and the core is small. Finally, the negative contribution from the cross term, that couples layer, core, and glass, has to be noted. The quality of the fit decreases substantially if  $S_2(Q)$  is not inserted in the fitting function (3). The contrast and correlation length values extracted from the fit through equation (3) are displayed in figure 3, each as a function of  $T$ . The fact that the  $T$ -dependence of the contrasts is not very strong suggests that only a small variation of the composition occurs in the pore in this range of  $T$ . The main difference between the two samples consists in the opposite signs of the contrasts. On combining these values with the characteristics of the mixture, it can be established that layer B, which is coating the pore wall, is the phase richer in hexane. Also, the evaluation of the ratio between  $K_{BA} = \rho_B - \rho_A$  and the initial absorbed value  $\rho$  gives the percentage variation between the layer and core concentration with respect to the free case. It turns out that for #H the concentration varies by  $\sim 10\%$ , while for #D it varies by  $\sim 2\%$ ; therefore both samples, but mainly #D, were still close to the initial critical concentration.

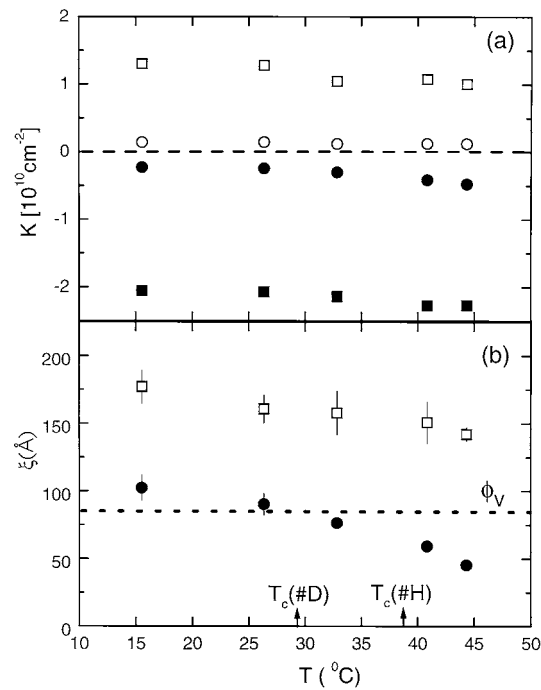
The results for  $\xi$  shown in figure 3 reinforce this observation; as a reference, the corresponding bulk critical temperatures and the value of  $\phi_v$  are also reported. The  $\xi$ -values,

$\dagger$  In other words,  $S_2(Q)$  represents a virtual dry Vycor structure factor with a smaller pore diameter (as obtained with  $\rho_B = \rho_V$  in the pore representation of figure 1).



**Figure 2.** The intensity scattered from #D at the lowest  $T$  (full squares), compared with the result of the fit to the data through equation (3). The symbols indicating the different components of the fit are shown in the key.

even though large, do not display the typical behaviour occurring close to the bulk critical point, where they rapidly diverge; a critical point, if it exists, is shifted to temperatures much lower than  $T_{bc}$ , as predicted. Similarly to the contrast behaviour,  $\xi$  increases smoothly when  $T$  decreases: therefore phase separation does not occur as found for #HD, at least in the  $T$ -range explored. As no evidence of a LSQ term was found, at present it is not possible to conclude as to whether the transition from this behaviour to the phase separation observed in #HD follows the RFIM predictions, or develops differently. Our findings suggest however that the single-pore model would not always be adequate; it is probably inadequate in cases where the host interaction with the fluid is not sufficient to remove the possibility that long-range order takes place. The concentration fluctuations occurring in the two samples may exceed  $\phi_v$ , which therefore does not represent a cut-off length for the extent of critical fluctuations. Correlation lengths are always larger in #D than #H, confirming that in the former the concentration was closer to the bulk critical one. We may note that a correlation length lower than the pore diameter, such as occurs for #H at high  $T$ , corresponds to a stronger  $T$ -dependence of  $\xi$ , and when  $\xi$  becomes of the order of  $\phi_v$  the correlation lengths increase similarly for the two samples. As shown in [7], it is not possible to evaluate the layer thickness on the basis of the second peak position. It is reasonable to assume that the absorbed layer consists of a thin film blocked on the pore wall, while fluctuations may take place in the inner free fluid because it is not far away from critical conditions. Even if it is not possible to be conclusive on the basis of a few experimental points, the main effect of the pore size seems to lie in a smearing of the distribution of  $\xi$ , but the fluctuations remain free to extend also over more pores.



**Figure 3.** Fit parameters relating to #H (full symbols) and #D (open symbols) as functions of  $T$ . In (a) the contrasts  $K_{BV}$  (square) and  $K_{BA}$  (circles) are shown, while the dashed line indicates the zero level.  $\xi$ -data are reported in (b), and compared with the mean pore diameter  $\phi_v$  (dashed line); two arrows mark the two bulk critical temperatures.

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