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# Condensation of helium in aerogels as an experimental realization of the out-of-equilibrium Random Field Ising Model

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## Abstract

The zero temperature out-of-equilibrium dynamics of the Random Field Ising Model has been predicted by Sethna *et al.* to present two regimes. While macroscopic magnetization loops are smooth above a critical disorder, they exhibit finite jumps below. Combining thermodynamic and optical measurements, we show that the condensation of  $^4\text{He}$  in base-catalysed silica aerogels of large porosity presents a similar out-of-equilibrium behavior when the temperature, rather than the disorder, is varied. Our experiment provides the first observation of the Sethna *et al.* theory in a non-magnetic system.

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The effect of disorder on a first order phase transition is a fundamental question in statistical physics. Its difficulty stems from the fact that disorder often generates a complex free energy landscape presenting multiple metastable states, which might make the phase transition unobservable. Many studies have addressed this problem by studying the Random Field Ising Model (RFIM), where disorder is added through a local random field on each site of the Ising model. In this framework, Sethna *et al.* [1, 2] have shown that, in the zero temperature limit, where the barriers induced by disorder cannot be overcome by thermal activation, disorder gives rise to a specific *out-of-equilibrium* behavior. As the external field  $H$  is swept up, the magnetization  $M$  then reverses from negative to positive by a series of avalanches, corresponding to flips of spin clusters taking place for specific values of  $H$ . Remarkably, Sethna *et al.* find that a critical disorder exists below which the largest avalanche becomes macroscopic. Correspondingly, the  $M(H)$  curve which is smooth above the critical disorder, presents an abrupt portion below. Although this change of shape is similar to that expected for the *equilibrium* paramagnetic-ferromagnetic transition (which, within the RFIM, is predicted to survive to a weak enough disorder [3]), its origin is totally different.

A review paper by Sethna *et al.* [4] lists a wide variety of systems in which avalanches are observed. However, the supposedly universal transition between the micro- and the macro-avalanches regimes has only been experimentally observed once, by Berger *et al.* [5], who measured the expected change of shape in the  $M(H)$  curves of a thin Cobalt film. Their system is however complex as the disorder results from the exchange coupling to an antiferromagnetic CoO overlayer. In this Letter, we show that the liquid-vapor transition of  $^4\text{He}$  confined in very porous gels exhibits the behavior predicted by the Sethna *et al.* scenario. This is its first observation in a non-magnetic system, free of the complexity induced by the random exchange and/or the dipolar effects present in the magnetic systems.

The idea that the liquid-gas transition and the phase separation of binary mixtures inside disordered porous gels are experimental realizations of the RFIM has first been put forward by Brochard and de Gennes [6]. In these Ising-like systems, the preferential attraction of the disordered substrate for one fluid phase provides the random field, and the fluid 1/fluid 2 interfacial energy is the equivalent of the coupling between spins. In the liquid/gas case, the analog of the  $M(H)$  curve is  $\Phi(\mu)$ , where  $\Phi$  is the liquid fraction, and  $\mu$  the chemical potential. Kierlik *et al.* introduced a disordered lattice-gas model solved by using a local

mean-field theory to compute  $\Phi(\mu)$  for condensation of fluids confined in porous materials neglecting any thermal activation [7]. Applying this model to gels (numerically synthesized by diffusion cluster limited aggregation or DLCA), shows that  $\Phi(\mu)$  presents, as a function of porosity, a change of shape similar to that predicted within the zero temperature RFIM as a function of disorder [8]. Moreover, for a given, weak enough, disorder, they predict a similar change as a function of temperature  $T$  [9] (through the temperature dependence of the energy landscape). This can be qualitatively understood as being the effect of tuning, through the temperature dependence of the interfacial energy, the relevant parameter of the transition, which, in the magnetic case, is the ratio of the disorder strength to the spin coupling [1].

Silica aerogels grown in basic pH are an experimental realization of DLCA gels [10]. In contrast to other fluids [11],  $^4\text{He}$ , thanks to its low surface tension, can be condensed in these highly compressible materials without deforming them [12], providing an opportunity to test Kierlik *et al.* numerical predictions [8, 9]. Previous experiments have shown that the condensation isotherms  $\Phi(P)$  (the pressure  $P$  being related to  $\mu$ ) become steeper with increasing porosity [13] or decreasing temperature [13–15], qualitatively consistent with these predictions. In the present study, we use an improved experimental set-up to demonstrate that this behavior is indeed the signature of the transition predicted by the Sethna *et al.* model.

We synthesized two aerogels by a one-step process at basic pH = 9 [16]. Their porosities are 95% (density 102 g/L, B102) and 98.5% (35 g/L, B35). The samples were grown as 3.7 mm thick, 13 mm diameter cylinders between Teflon plates to obtain surfaces of good optical quality, and moved to a copper cell closed by two sapphire windows. Condensation of  $^4\text{He}$  in these samples is studied in an optical cryostat for  $T$  between 4.4 K and  $T_c \approx 5.2$  K. The cell temperature is regulated within 10  $\mu\text{K}$ . Condensation is performed at a fixed flowrate by heating between 80 K and 180 K an external reservoir connected to the cell [17]. Typical condensation time is 10 to 20 h, long enough for the isotherm shape to be independent of the flowrate. The pressure  $P$  is measured at room temperature by a pressure gauge connected to the cell by a separate capillary, with a resolution of 10  $\mu\text{bar}$ . The amount of  $^4\text{He}$  inside the aerogel, computed by subtracting the contents of the external reservoir and of the dead volumes from the total known amount in the system, is converted to a global liquid fraction  $\Phi$  as described elsewhere [15].

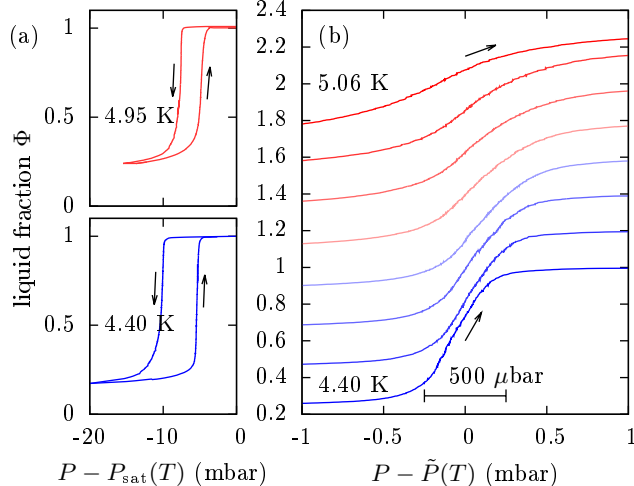


FIG. 1. (a) Hysteresis between adsorption and desorption isotherms at  $T = 4.40$  K and 4.95 K. (b) Adsorption isotherms for  $T = 4.40$  K, 4.50 K, 4.60 K, 4.70 K, 4.80 K, 4.90 K, 4.95 K and 5.06 K.  $\tilde{P}(T)$  is the pressure at which the slope of the isotherm is maximum. The y scale applies to the 4.40 K curve, the other curves are vertically shifted by 0.2 for clarity.

Figure 1(a) shows the full hysteresis loop for B102 at 4.40 K and 4.95 K. The condensation branch is steeper at the lower temperature, confirming with a much better accuracy the results previously reported for a sample of similar porosity [15]. Figure 1(b) resolves in detail this evolution when  $T$  decreases from 5.06 K to 4.40 K. The increasing steepness cannot be explained by a classical model of capillary condensation, with a temperature independent pore size distribution [18]. Such a model would predict little change in the shape of the adsorption isotherm, as indeed observed for condensation of helium in Vycor [19]. In contrast, it is consistent with the behavior predicted by the Kierlik *et al.* model as its critical temperature is approached from above. At the lowest temperature studied, the slope remains finite, the aerogel filling over a range of 500  $\mu\text{bar}$ . As we now show, this finite width is an artifact resulting from the heterogeneity of our sample. Optical measurements, by locally probing the condensation process, reveal that it takes place abruptly below 4.7 K.

Figure 2(a) shows our optical set-up. The sample is illuminated with a 50  $\mu\text{m}$  wide HeNe laser sheet at a  $45^\circ$  angle with respect to the disk axis, and the thus defined slice is imaged at  $45^\circ$  and  $135^\circ$  from the incident direction. Figure 2(b) shows the same slice for increasing values of  $\Phi$  for two temperatures [20]. In both cases, at low liquid fraction, or for the fully filled sample, the small and uniform brightness is due to the silica background

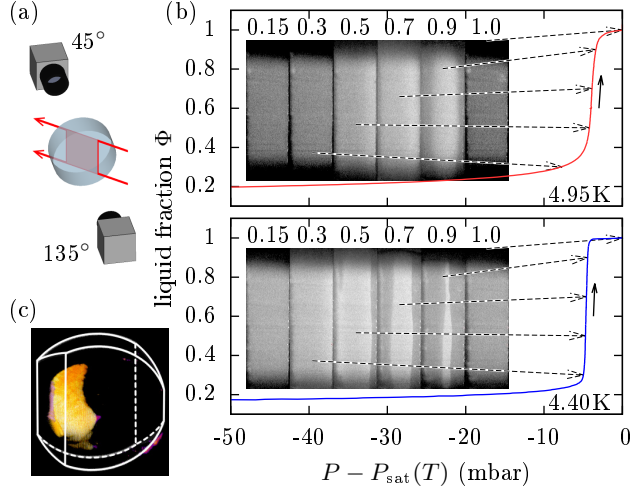


FIG. 2. (color online) (a) Positions of the laser sheet and of the CCD cameras relative to the aerogel. (b) Pictures taken with the  $135^\circ$  CCD (logarithmic grayscale) at increasing liquid fractions (given above the pictures) during isotherms at  $T = 4.40$  K and  $4.95$  K. The arrows show the corresponding points on the isotherms. (c) Perspective view of a 3D tomographic reconstruction of  $I_{135}$  close to the end of the condensation isotherm at  $4.6$  K. The bright region, i.e. the not yet filled part of the aerogel, is located in its left part.

scattering. When approaching the steep part of the condensation isotherm, the scattered signal starts to grow, showing that the fluid density becomes heterogeneous at the scale of the optical wavelength [15]. At  $4.4$  K, above  $\Phi \approx 0.3$ , the pictures become macroscopically heterogeneous: the central bright region is surrounded by a darker region corresponding to the fully filled state of the aerogel. This shows that the aerogel does not fill uniformly. As more  $^4\text{He}$  is added to the cell, the bright region recesses. Translating the laser sheet parallel to itself evidences that the bright region always collapses in the same outer part of the aerogel when  $\Phi \rightarrow 1$  (Fig. 2(c)). This implies that the non uniform condensation does not result from fluid transport from the surface to the center of the sample, but from some heterogeneity of the sample.

We locally study the condensation process by measuring, as a function of  $P$ ,  $I_{135}$ , the signal scattered at  $135^\circ$  from a region corresponding to one CCD pixel [21]. Taking into account the pixel size and the width of the laser sheet, this corresponds to a parallelepipedic region about  $50 \mu\text{m}$  wide and high, and  $70 \mu\text{m}$  deep. This is much smaller than the disk size, but much larger than the aerogel microscopic scales (the silica correlation length is

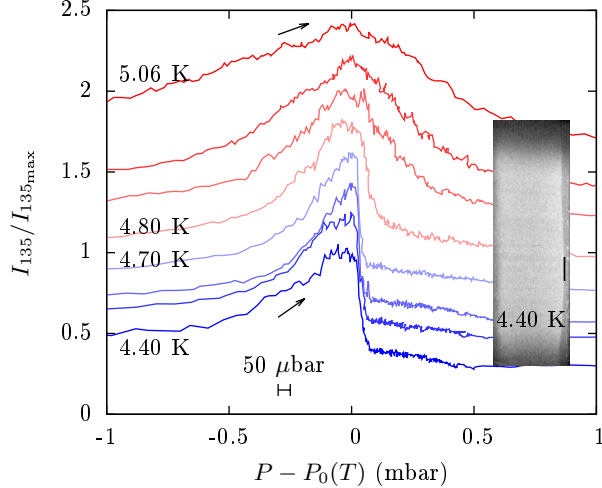


FIG. 3. (color online) Intensity scattered at  $135^\circ$  from the region marked by a black rectangle during condensation at the temperatures of Fig. 1(b).  $P_0(T)$  is the pressure at which the optical signal is maximum for a given temperature. The y scale apply to the 4.40 K curve, the other curves are vertically shifted by 0.2 for clarity.

estimated around 20 nm [22]). In practice, because the probed region is locally homogeneous in the vertical direction, we improve the signal-to-noise ratio by averaging  $I_{135}$  in a vertical rectangle about 1 mm high.  $I_{135}$  depends on both the local liquid fraction  $\varphi$  *in the volume thus defined*, and its spatial structure. By definition, the average of  $\varphi$  over the sample is  $\Phi$ . Qualitatively, as condensation locally proceeds, one expects liquid microdroplets to appear and increase in size, up to a point where the situation is better described in terms of vapor microbubbles decreasing in size and number. We thus expect  $I_{135}$  to present a maximum as a function of pressure as  $\varphi$  increases from 0 to 1.

The pressure dependence of  $I_{135}$ , shown in Fig. 3, evidences two different regimes of condensation as a function of temperature. For  $T > 4.80$  K,  $I_{135}$  increases as a function of pressure up to  $P_0(T)$ , where the optical signal is maximum, then decreases continuously, as expected for a continuous condensation process. In contrast, for  $T < T^* = 4.70$  K, the continuous increase of  $I_{135}$  up to  $P_0$  is followed by a sharp decrease down to the filled state value [23]. The same behavior is observed at any position in the illuminated slice, except that  $P_0$  varies by about  $500 \mu\text{bar}$  across the sample. Convoluting this spatial variation with the size of the optically probed region accounts for the finite width ( $30\text{--}40 \mu\text{bar}$ ) over which  $I_{135}$  drops in Fig. 3. Our measurements are therefore consistent with *abrupt local* condensation

isotherms below  $T^*$ .

In the spirit of ref. [24], this observation, together with the coexistence of bright and dark regions in Fig. 2, could be interpreted in terms of a genuine first order *equilibrium* phase transition between a gas-like phase (inside the bright region) and the liquid phase.  $T^*$  would then be the critical temperature of this transition, shifted below  $T_c$  due to disorder. However, this hypothesis cannot explain the hysteresis between condensation and evaporation above  $T^*$ . In contrast, our observations are accounted for by  $T^*$  being the critical temperature of the Kierlik *et al.* model.

Our results for the lighter sample B35 confirm this scenario. Macroscopic isotherms show that condensation takes place much closer to the bulk saturation pressure than for B102 (1 mbar versus 5 mbar at 4.5 K), over a narrow pressure interval (less than 100  $\mu$ bar) up to close to  $T_c$ . An analysis of the optical measurements similar to Fig. 3 reveals that the condensation process is abrupt up to  $T^*$  lying between 5.0 K and 5.1 K. Both the smaller pressure shift and the larger  $T^*$  value are in agreement with the predicted influence of porosity on the out-of-equilibrium critical temperature [9].

In the following, we exploit our experimental system to discuss the physical origin of the macroscopic avalanche observed below  $T^*$ . Transposing to our case the ideas of ref. [25] for the  $T = 0$  RFIM, we can speculate that starting from an empty aerogel, the condensation isotherm follows the outer envelop of the distribution of metastable states in the  $(P, \varphi)$  plane. A macroscopic jump of  $\varphi$  then occurs if this distribution is reentrant, as illustrated in Fig. 4(c). In this case, filling from a not fully empty initial state could suppress the jump. We have checked that this is indeed the case by performing minor hysteresis loops and monitoring the optical signal at a given position inside the aerogel. Figure 4(a) shows pictures taken along such a loop at 4.60 K ( $< T^*$ ). Starting from the empty state, we increase the pressure up to  $P_B$ , where the dot in Fig. 4(a) is just filled (picture B), then decrease it until the dot starts to empty, as indicated by the increased local brightness (picture D), then fill it again up to  $P_B$  [26]. Figure 4(b) compares the intensity scattered by the dot for the two different condensation paths (from  $P_{\text{empty}}$  to  $P_B$  and from  $P_D$  to  $P_B$ ). When starting from  $P_D$ , the dot signal continuously decreases to the liquid state value, with no jump in contrast to what observed when filling from the fully emptied state. This dependence of the condensation process on the path followed within the  $(P, \varphi)$  plane is consistent with the hypothesis of the jump being due to a reentrant distribution of metastable states [25].



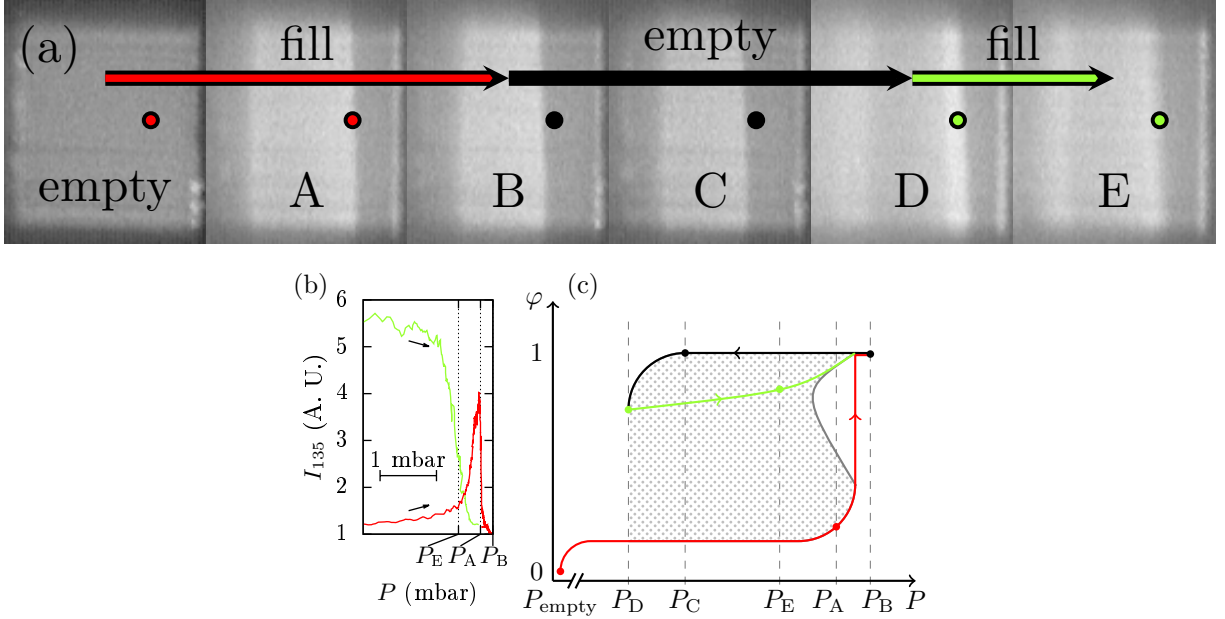


FIG. 4. (color online) (a) Central parts of pictures taken along a minor hysteresis loop at  $T = 4.6$  K ( $< T^*$ ). (b) Optical signal from the dot in Fig. 4(a) when increasing  $P$  from  $P_{\text{empty}}$  to  $P_B$  (red/dark) and from  $P_D$  to  $P_B$  (green/grey). (c) Hypothetical distribution of metastable states (shaded area, only shown for  $P > P_D$ ) in the  $(P, \varphi)$  plane, and paths deduced from the local optical signal in Figs. 4(a) and (b).

What could be the physical origin of this reentrance? A simple picture would be that it follows from a capillary instability of the microscopic liquid-vapor menisci connecting neighboring silica strands, taking place for a well-defined liquid fraction  $\varphi$ . This would be consistent with the behavior observed at a given temperature: the value of  $I_{135}$  just before full condensation (i.e. the maximum of  $I_{135}$  in Fig. 3) is the same across the aerogel width, suggesting that the avalanche threshold corresponds to a statistically similar distribution of liquid microdomains, hence a given value of  $\varphi$ . However, this value of  $\varphi$  depends on temperature, as the corresponding  $I_{135}$  signal, once corrected for the effect of the temperature dependent optical contrast between liquid and vapor [15, 19], increases with  $T$  up to  $T^*$ . This implies that the macroscopic avalanche starts for different geometric fluid configurations at different temperatures. We have characterized the size of the liquid microdomains just before the avalanche by the anisotropy of scattering, measured by the ratio of the intensities scattered at  $45^\circ$  and  $135^\circ$ , after subtraction of the silica background [27]. This ratio increases

from 2 at 4.40 K up to 5 at 4.70 K, showing that the size of the liquid microdomains at the avalanche threshold increases with  $T$ , in contrast to the expectation for a simple capillary instability, but in agreement with preliminary simulations within the Kierlik *et al.* model. This dependence should be accounted for by any future physical explanation of the macroscopic avalanche.

In conclusion, condensation of  $^4\text{He}$  in silica aerogels presents the out-of-equilibrium critical point [28] predicted by the local mean field approach [8, 9]. Our result leads to revisit earlier experiments on condensation of fluids [24, 29] or phase separation of binary fluids [30] in aerogels, where a change of the isotherms shape from abrupt to smooth has been reported at a temperature  $T^* < T_c$ . While such a change has previously been interpreted in terms of a disorder-shifted genuine critical point, we suggest that it could rather correspond, similarly to our case, to an out-of-equilibrium critical point. This naturally explains the slow dynamics observed above  $T^*$  in these systems, as, in the out-of-equilibrium scenario, hysteresis is observed on both sides of  $T^*$ . If this interpretation is correct, the Sethna *et al.* [1] mechanism could be more general than reported up to now.

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- [26] Note that the different brightness of the dot for pictures A and D shows that the non fully filled state differs between condensation and evaporation, confirming that it does not correspond to a well defined equilibrium phase.
- [27] This quantity is measured, without any error due to attenuation, at the last pressure where the bright domain intersects the illuminated section.
- [28] Unlike Berger *et al.*, we have not attempted to measure critical exponents for the isotherm shape close to the transition. The aerogel heterogeneity broadens the macroscopic isotherms,

while, locally, it is not possible to quantify the local liquid fraction from the scattered signal.

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