Condensation of Helium in Aerogel and Athermal Dynamics of the Random-Field Ising Model

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High resolution measurements reveal that condensation isotherms of ^{4}He in high porosity silica aerogel become discontinuous below a critical temperature. We show that this behavior does not correspond to an equilibrium phase transition modified by the disorder induced by the aerogel structure, but to the disorder-driven critical point predicted for the athermal out-of-equilibrium dynamics of the random-field Ising model. Our results evidence the key role of nonequilibrium effects in the phase transitions of disordered systems.

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The Ising model has a central role in statistical physics. At the root of the critical scaling concept in clean systems, it is also a prototype to study the effect of disorder on phase transitions. In the random-field Ising model (RFIM), the key question is whether a random local magnetic field acting on the Ising spins destroys the order induced by the spin coupling. After years of fierce theoretical debate, it is now accepted that, in three dimensions and at low temperature, an ordered phase should exist below a critical disorder strength [1]. The experimental situation is not that clear cut. In magnetic systems, the mixing of random-field and random exchange effects makes the situation complex. As proposed thirty years ago [2,3], the condensation (or the demixion) of (binary) fluids in disordered porous media should offer an alternative testing ground for the theory. Indeed, the pure Ising model and the liquid-vapor (or demixing) transition fall in the same universality class, and the preferential attraction of the substrate for one phase is equivalent to the effect of a random field. However, while early experiments conducted in Vycor, a porous glass, were originally interpreted in terms of a random-field transition [4–6], the observations could also be accounted for by wetting effects in a confined, nonrandom, geometry [7]. Subsequently, a breakthrough came when Wong and Chan measured in 1990 the condensation isotherms of helium in very porous silica aerogels, and found that their shape changed from discontinuous to continuous at a temperature below the bulk critical temperature [8]. The same behavior has been observed for the condensation of nitrogen [9], and the demixion of binary fluids inside silica gels [10], and similarly interpreted in terms of the equilibrium behavior of the RFIM. But, although these results still greatly influence present research [11], further studies demonstrated that the condensation of helium in aerogels is reversible only very close to the bulk critical temperature, in which case the condensation isotherms are always smooth [12,13]. A steepening of the isotherms was only observed at lower temperatures [14], where condensation and evaporation are strongly hysteretic, raising the question whether the equilibrium state is really reached. In fact, these observations have been suggested [15] to result from a totally different phenomenon, introduced by Sethna *et al.* [16,17] for the RFIM, and extended to condensation of fluids in highly porous random materials by Kierlik *et al.* [18], namely, the occurrence of an out-of-equilibrium *disorder-driven critical point*. In this Letter, we report experiments which demonstrate the reality of this new paradigm.

The key feature of the Sethna *et al.* theory [16,17] is to consider the RFIM model in the athermal limit, where the disorder-induced barriers cannot be overcome by thermal activation. As the external field H is swept up, the magnetization M then reverses from negative to positive by a series of avalanches [19], corresponding to flips of spin clusters taking place for specific values of H. Remarkably, below a critical value for the ratio of disorder strength to spin coupling, the largest avalanche becomes macroscopic. Correspondingly, the $M(H)$ curve which is smooth above the critical disorder, presents a jump below. Although similar to the one occurring at an *equilibrium* paramagnetic-ferromagnetic critical point, this change of shape has a totally different origin, which Sethna *et al.* emphasize by using the term of *disorder-driven critical point*. Although in principle universal, disorder-driven critical points have only been experimentally reported in two magnetic systems [20,21]. In both cases, however, the critical exponents deduced from a scaling analysis of the $M(H)$ curves differ from the values predicted for the 3D athermal RFIM [22]. As in the equilibrium case, this may result from the presence of antiferromagnetic interactions [21].

A Sethna *et al.*-like transition has been predicted for condensation of fluids confined in random disordered porous materials by Kierlik *et al.* [18]. Using a local mean-field approach, these authors show that the analog of the magnetization curve, the condensation isotherm $\Phi(P)$ (where Φ is the liquid fraction and P the pressure), presents a change of shape similar to the one predicted within the athermal RFIM for decreasing disorder [23]. It takes place when increasing the porosity [23] or decreasing the temperature at constant, large enough, porosity [24]. In this Letter, we observe such a *disorder-driven* transition for the condensation of helium into a high porosity aerogel (95% porosity, density 102 g/L) synthesized by a one-step process at $p\mathrm{H} = 9$ [25,26]. We obtain four major results: (i) using optical means to resolve on a local scale the condensation process, we evidence the predicted transition from discontinuous (vertical) to smooth isotherms; (ii) we demonstrate unambiguously the *nonequilibrium* nature of this transition; (iii) in agreement with theory, the occurrence of the transition depends on the pressure history; (iv) in contrast to simple expectation, the macroscopic avalanche does not follow from some purely geometric capillary instability [3].

Our aerogel was grown as a 3.7 mm thick, 13 mm diameter cylinder between Teflon plates to obtain surfaces of good optical quality, and moved to a copper cell closed by two sapphire windows. Condensation of ^{4}He is studied in an optical cryostat between 4.4 K and the bulk critical temperature, $T_c \approx 5.2$ K. The cell temperature is regulated within 10 μK. The temperature heterogeneity within the aerogel resulting from the absorption of the 300 K infrared radiation transmitted through the cryostat windows is estimated smaller than 1 μK [27]. Blocking this IR radiation using shutters thermalized at 4 K has no influence on the isotherms, nor on our optical measurements [27]. Condensation is performed at a fixed flow rate by heating between 80 and 180 K an external reservoir connected to the cell [28]. The typical condensation time is 10 to 20 h, long enough for the isotherm shape to be independent of the flow rate. P is measured at room temperature by a pressure gauge connected to the cell by a separate capillary, with a resolution of 10 μbar. The amount of ^{4}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 Φ as described elsewhere [15].

Figures 1(a) and 1(b) show the full hysteresis loop at 4.40 and 4.95 K, and details of its condensation branch for T decreasing from 5.06 to 4.40 K. The isotherms become steeper as the temperature decreases, but their slope saturates at low temperature: at 4.40 K, the aerogel fills over a range of 500 μbar. As shown by optical measurements, this finite width results from the macroscopic heterogeneity of our sample, which masks a disorder-driven transition occurring close to 4.7 K.

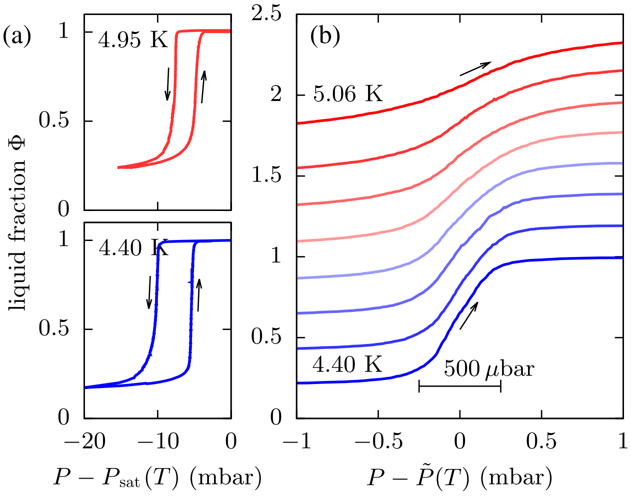

FIG. 1 (color online). (a) Hysteresis between adsorption and desorption isotherms at $T = 4.40$ and 4.95 K. $P_{\mathrm{sat}}(T)$ is the bulk vapor pressure. (b) Adsorption isotherms for $T = 4.40$, 4.50, 4.60, 4.70, 4.80, 4.90, 4.95, and 5.06 K. $\tilde{P}(T)$ is the pressure at which the slope of the 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 2(a) shows our optical setup. The sample is illuminated with a 50 μm thick HeNe laser sheet at a 45° angle with respect to the cylinder axis, and the thus defined slice is imaged at 45° and 135° from the incident direction. Figure 2(b) shows the same slice for increasing values of Φ for two temperatures [29]. In both cases, at low liquid fraction, or for the fully filled sample, the small and uniform brightness is due to the silica background 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 4.40 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}He is added to the cell, the bright region recesses. Scanning the aerogel with the laser sheet evidences that the bright region always collapses in the same outer part of the aerogel when $\Phi \to 1$ [Fig. 2(c)]. This implies that the nonuniform condensation does not result from fluid transport from the surface to the center of the sample, but from some heterogeneity of the sample.

(i) Transition from vertical to smooth isotherms.—We locally study the condensation process by measuring, as a function of P, I_{135}, the signal scattered at 135° from a region corresponding to one CCD pixel [30]. Taking into account the pixel size and the laser sheet thickness, this corresponds to a parallelepipedic region about 50 μm wide and high, and 70 μm deep. This is much smaller than the sample size, but much larger than the aerogel microscopic

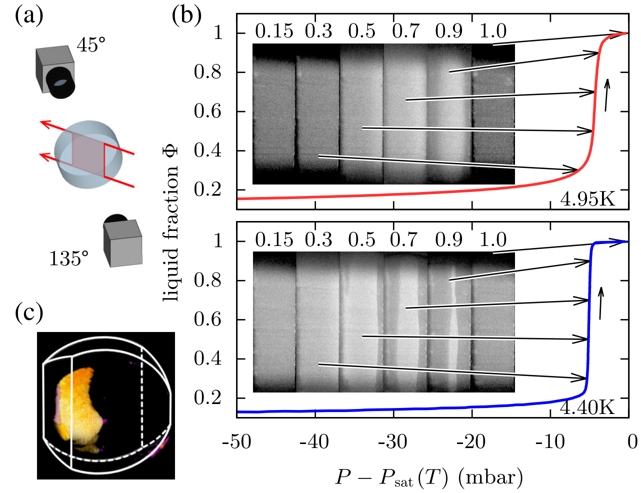

FIG. 2 (color online). (a) Positions of the laser sheet and of the CCD cameras relative to the aerogel. (b) Pictures of the illuminated region (1 cm height) taken with the 135° CCD (logarithmic gray scale) at increasing liquid fractions (given above the pictures) during isotherms at $T = 4.40$ and 4.95 K. The arrows show the corresponding points on the isotherms. (c) Perspective view of a 3D tomographic reconstruction (see text) close to the end of the condensation isotherm ($\Phi \approx 0.95$) at 4.60 K. The bright region, i.e., the not yet filled part of the aerogel, is located in its left part.

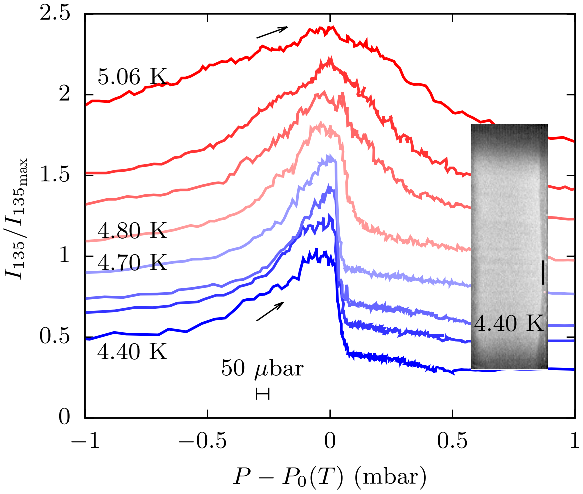

FIG. 3 (color online). Intensity scattered at 135° (from the region marked by a black rectangle on the inset picture) during condensation at the temperatures of Fig. 1(b). $P_0(T)$ is the pressure at which the optical signal is maximum at a given temperature. The y scale applies to the 4.40 K curve,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

scales (the silica correlation length is estimated around 10 nm [15]). 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 φ *in the volume thus defined*, and the spatial fluid configuration. Qualitatively, as condensation locally proceeds, one expects liquid microdomains to appear and increase in size, up to a point where the situation is better described in terms of vapor microdomains decreasing in size and number. We thus expect I_{135} to present a maximum as a function of pressure as φ 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 $T \geq 4.80$ K, I_{135} increases as a function of pressure up to $P_0(T)$, the pressure of its maximum, then decreases continuously, as expected for a continuous condensation process. In contrast, for $T \leq 4.70$ K, the continuous increase of I_{135} up to P_0 is followed by a sharp decrease down to the filled state value [31]. The same behavior is observed at any position in the illuminated slice, except that P_0 varies by about 500 μbar across the sample. Convolving this spatial variation with the size of the optically probed region accounts for the finite width (30–40 μbar) over which I_{135} drops in Fig. 3. Our observations are therefore consistent with *abrupt local* condensation isotherms below a temperature T^* ($4.70\ \text{K} \leq T^* < 4.80$ K). Measurements for intermediate temperatures show that $4.700\ \text{K} \leq T^* \leq 4.725$ K (data not shown).

(ii) Nonequilibrium nature of the transition.—In the spirit of Ref. [8], this change of shape, together with the coexistence of bright and dark regions in Fig. 2, could be interpreted in terms of a first order *equilibrium* phase transition between a gaslike phase (inside the bright region) and the liquid phase. In this interpretation, T^* would be the transition critical temperature, shifted below T_c due to disorder, while the observed hysteresis would be explained by the pinning of the macroscopic interface between the two presumed phases. Hysteresis should then be absent *above* T^*, where the concept of interface has no meaning. This is not the case as hysteresis is observed up to 5.16 K, well above T^* [13]. Moreover, optical measurements show that the fluid distribution in the gaslike region is not the same on condensation and evaporation, directly showing that this region does not correspond to a true thermodynamic phase. This is illustrated by Fig. 4(a) which shows pictures taken at 4.60 K ($< T^*$) when reverting from condensation to evaporation before the aerogel is fully filled. Starting from the empty state, we condense up to the pressure P_B, where the dot in Fig. 4(a) is just filled (picture *B*), then evaporate by decreasing the pressure. In the interpretation of a pinned interface, one would expect, once the pressure reaches the pressure P_D of the evaporation branch of the full hysteresis loop, the interface to move backwards, retracing in reverted order the same states than during filling. This is not observed. At P_D, when the dot starts to empty, its state differs from the state upon filling, as indicated by the increased local brightness [picture *D* and Fig. 4(b)]. This set of results excludes that the abrupt condensation below T^* corresponds to an equilibrium phase transition.

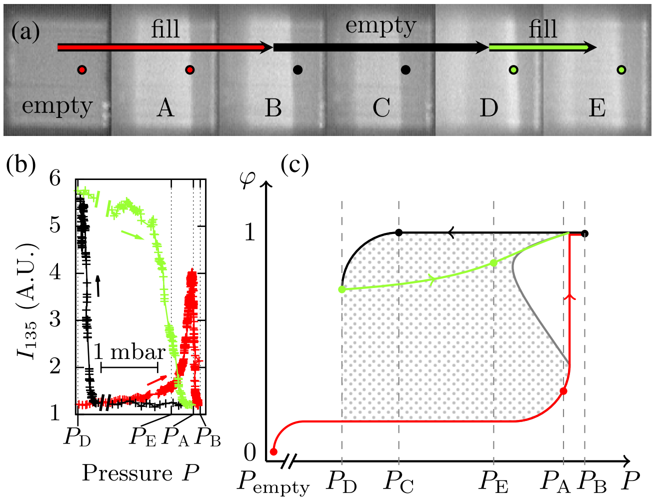

FIG. 4 (color online). (a) Central parts of pictures taken along a minor hysteresis loop at $T = 4.60$ K ($< T^*$). (b) Corresponding optical signal from the dot in (a) as a function of pressure. In chronological order, red (dark gray) is the initial filling; black shows partial emptying; green (light gray) is filling from the partially emptied state. (c) Hypothetical distribution of metastable states (shaded area, only shown for $P > P_D$) in the (P, φ) plane, and paths deduced from the local optical signal in (a) and (b).

(iii) History dependence.—We now identify this phenomenon to the out-of-equilibrium transition predicted by Sethna *et al.* by studying its dependence on history. From results on the athermal RFIM on a random graph [32], one expects that, starting from an empty aerogel, a macroscopic jump of φ follows from a reentrance of the outer envelope of the distribution of metastable states in the (P, φ) plane, as, for this initial condition, condensation proceeds along this envelope. For such a distribution, illustrated in Fig. 4(c), filling from an only partly emptied initial state should suppress the jump. As shown by Fig. 4(b), this is indeed the behavior observed for the dot of Fig. 4(a): when starting from P_D, where it was only partly emptied, the dot continuously fills (its scattered signal continuously decreases to the liquid state value, unlike what is observed when filling from the fully emptied state).

(iv) Microscopic origin of the abrupt condensation.—At 4.7 K, liquid and gas can be discriminated on the scale of the aerogel correlation length. One could then interpret the abrupt condensation below T^* as a capillary instability of the microscopic liquid-vapor menisci connecting neighboring silica strands, a scenario first introduced by de Gennes [3]. The abrupt condensation event should then take place for a given menisci configuration, independently on temperature, hence, for a given average size of the liquid microdomains. This is not the case. While, at a given temperature, the value of I_{135} just before full condensation (i.e., the value of $I_{135_{\mathrm{max}}}$ in Fig. 3) is the same across the aerogel width consistent with the macroscopic avalanche occurring for a given average size of the liquid microdomains, this size depends on temperature. To show it, we have measured the scattering anisotropy, as given by the ratio of the intensities scattered at 45° and 135°, after subtraction of the silica background [33]. This ratio increases from 2 at 4.40 K up to 5 at 4.70 K, implying that the size of the liquid microdomains at the avalanche threshold increases with temperature. This behavior is in qualitative agreement with preliminary simulations within the Kierlik *et al.*'s model [34].

Conclusion.—Our measurements demonstrate that, despite the finite temperature, the concept of athermal, out-of-equilibrium, dynamics accounts for the process of fluid condensation into our 95% porosity aerogel. We confirmed the universal character of this concept by measurements on a lighter (98.5%) aerogel (see Supplemental Material [35]). The larger value of T^* measured in this case agrees with the theoretical expectation that T^* increases when disorder decreases [36]. Our results lead us to revisit earlier experiments [8–10] where a change of the isotherms shape has been interpreted in terms of a disorder-shifted equilibrium critical point. Similarly to our case, it could rather result from an out-of-equilibrium critical point. As hysteresis occurs on both sides of T^* in the out-of-equilibrium scenario, this would naturally explain the slow dynamics reported above T^* in these experiments. While our results thus suggest that observing a true equilibrium behavior in RFIM-like disordered systems could be challenging, they also show the pertinence of nonequilibrium concepts to describe the properties of first-order phase transitions in the presence of disorder.

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[29] Note that the pictures only evolve when Φ increases and not if condensation is paused. This is similar to the spin flips of the athermal RFIM which only take place when the field is swept.

[30] The choice of 135° rather than 45° minimizes the attenuation of the scattered light due to propagation through the bright region.

[31] More precisely, the signal drops to a slightly larger value than the filled state value. This is a second-order scattering effect, due to the illumination of the filled aerogel by the recessing bright region.

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