

Evaporation of helium in a porous material

Porous materials are thirsty materials. Fluids whose liquid phase wets their substrate condense in porous materials at pressures smaller than the saturated vapour pressure, pressures where the bulk stable phase would be gaseous. For water, examples in everyday life range from the silica gels used as desiccants, to wood. Also, unlike in bulk conditions, the transition from gas to liquid shows strong hysteresis. Drying a porous material requires lowering the pressure well below the condensation pressure. Understanding the origin of the hysteresis, and the underlying evaporation mechanisms, is important for determining pore sizes distributions from the shape of the condensed mass vs pressure isotherms. In this work, we use a specific property of helium gas to demonstrate a crossover from a collective percolation evaporation mechanism to a local evaporation mechanism as the temperature is increased.

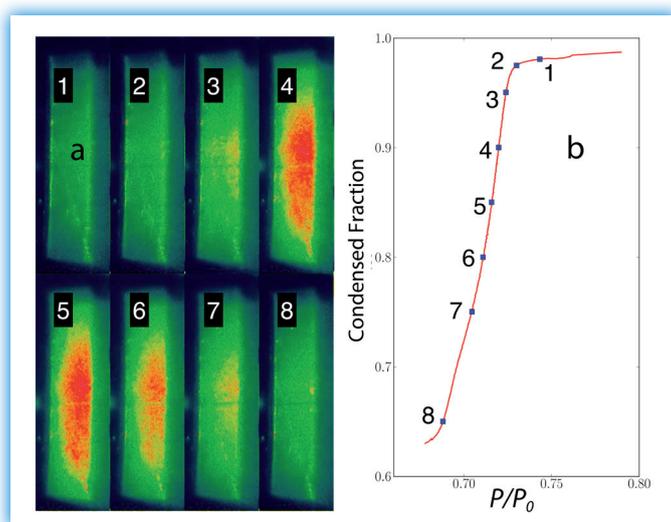


Fig. 1: Evaporation of helium in Vycor at 3 K. As pressure P is decreased below the saturated vapour pressure (P_0), the material empties. (a) Scattered-light images of a cross-section of the sample along the pressure isotherm of Fig. (b). The bright scattering signal is the signature of the collective nature of evaporation.

Condensation below the saturated vapour pressure is qualitatively explained by capillarity. In the same way as water rises in a thin straw, a fluid can condense in the narrow cylindrical channels of a porous material. The smaller the channel diameter, the lower the equilibrium pressure P_{eq} above which the liquid phase is stable.

Inversely, evaporation inside a channel open to the surface of the porous material can proceed at P_{eq} by recession of a liquid-gas meniscus inwards along the channel. However, in a disordered porous material, many of the pores are surrounded only by pores of smaller diameter. The bigger pores cannot empty at their equilibrium pressure as the neighbouring pores are filled with liquid, blocking the access to the vapour outside the sample. Evaporation must then proceed by one of two pathways, cavitation or percolation. Cavitation consists in the thermally activated local formation of a bubble. If cavitation cannot occur, and the pressure is decreased, all pores remain filled until potentially emptyable pores form a connected network (a percolation network) throughout the whole sample, at which point all these pores empty together.

It is expected theoretically that the evaporation mechanism should evolve from collective percolation to local cavitation as temperature increases, but experimental evidence for that has been scarce. In this work, we use light scattering to directly demonstrate the reality of this crossover.

Our porous material is a disk of Vycor, a porous silica glass with a topology similar to that of a sponge. Its interconnected pores are around 7 nm mean diameter and

30 nm in length, small enough for Vycor to be transparent to visible light. Our fluid is helium at temperatures below its critical point (5.2 K). Its extremely small refraction index (~ 1.02 at 3 K) allows us to use light scattering to probe the spatial distribution of the microscopic fluid. For other fluids of larger index, this would not be possible, as the large scattering would make the sample opaque, similar to a glass of milk.

Fig. 1(a) shows colour-coded images of the scattered light intensity in a cross-section of the disk. The sample is illuminated by a sheet of laser light propagating at a 45° angle with respect to the faces of the disk. Different images correspond to different stages of the evaporation process at a temperature of 3 K as the pressure P is lowered. This is to be compared with the remaining mass of liquid Helium inside the sample shown in Fig 1(b) as a function of pressure. The increased scattering brightness seen between points 2 and 7 implies that the fluid distribution is correlated over scales of distance much larger than the size of the pores, clear evidence for the expected collective effect. (At higher temperature, the scattering signal weakens and finally disappears, as local cavitation progressively sets in.)

Our result has practical consequences. The shape of condensation or desorption isotherms like those of Fig. 1(b) is widely used as a means to characterize pore-size distributions of porous materials, an important issue for many applications. This is based on the Barrett-Joyner-Halenda (BJH) theory, which assumes that pores empty independently at their size-dependent equilibrium pressure. For interconnected pores, this is at best an approximation. We are developing a model to establish criteria of approximate validity for the BJH method. Our experimental results will provide a benchmark for testing our approach.

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FURTHER READING

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

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