



# Improving sensitivity and accuracy of pore structural characterisation using scanning curves in integrated gas sorption and mercury porosimetry experiments



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## ABSTRACT

Gas sorption scanning curves are increasingly used as a means to supplement the pore structural information implicit in boundary adsorption and desorption isotherms to obtain more detailed pore space descriptors for disordered solids. However, co-operative adsorption phenomena set fundamental limits to the level of information that conventional scanning curve experiments can deliver. In this work, we use the novel integrated gas sorption and mercury porosimetry technique to show that crossing scanning curves are obtained for some through ink-bottle pores within a disordered solid, thence demonstrating that their shielded pore bodies are undetectable using conventional scanning experiments. While gas sorption alone was not sensitive enough to detect these pore features, the integrated technique was, and, thence, this synergistic method is more powerful than the two individual techniques applied separately. The integrated method also showed how the appropriate filling mechanism equation (e.g. meniscus geometry for capillary condensation equations), to use to convert filling pressure to pore size, varied with position along the adsorption branch, thereby enabling avoidance of the further systematic error introduced into PSDs by assuming a single filling mechanism for disordered solids.

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## 1. Introduction

The pore size distribution (PSD) is a key descriptor of heterogeneous catalyst pellets. It is used in the development of explanations for properties such as the observed catalyst activity under diffusion limited conditions. Nitrogen gas sorption at 77 K is a commonly used technique in industry for obtaining this descriptor in mesoporous materials. In a given mesopore, the gas sorption mechanism is generally thought to consist of initial build-up of adsorbed layers on the pore walls, and, at increased pressures, filling of the pore occurs by the process of capillary condensation [1]. On lowering the pressure, the process of capillary evaporation generally occurs at a lower pressure than for the corresponding pore-filling, and, thus, isotherms of mesoporous materials exhibit hysteresis and are classified as Type IV [1]. Gaining a proper understanding of this hysteresis has been a long-standing problem in studies of gas sorption, since it is required to decide which iso-

therm branch, and which analysis method, to use to determine an accurate PSD.

Scanning curve, and scanning loop, experiments have been suggested as a method to understand the hysteresis region of Type IV isotherms, and disambiguate the causes of hysteresis. For a general overview of scanning curves in gas sorption the reader is referred to earlier work by Tompsett et al. [2]. In gas sorption, scanning curves are achieved by reversing the progressive increase, or decrease, in pressure on the adsorption, or desorption, curve, respectively, while the sample is still partially saturated in the capillary condensation region. A desorption scanning curve is achieved when the direction of the change in pressure is reversed on the adsorption boundary curve, before the upper closure point of hysteresis has been reached. The analogous reversal in pressure on the desorption boundary curve, before the lower closure point of hysteresis has been reached, is termed an adsorption scanning curve. An early model, developed by Everett and Smith [3], and commonly referred to as independent domain theory, has been found to account for many of the findings. The main idea of the theory was that each pore space can fill and empty independently of the state of its neighbour. Therefore, for a set of open (through)

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pores that behave independently (see Section 2 for a detailed explanation), it is expected that desorption and adsorption scanning curves should cross directly from the adsorption and desorption boundary curves, respectively. Conversely, for pores that do not act independently, the scanning curves will meet the hysteresis loop at its closure point, or return back to the boundary curve. Previous work [4] has studied nitrogen desorption scanning curves for a set of controlled pore glasses (CPGs) and used independent domain theory to explain the findings. For some CPGs, the study found that the desorption scanning curves crossed directly between the boundary sorption curves. It was claimed that, since the desorption scanning curves crossed, the capillary condensation and evaporation events of nitrogen inside the interconnected pores of the CPGs take place independently of one another. However, more recently, Tompsett et al. [2] have theorised that desorption scanning curves can also cross when pore blocking effects occur. Moreover, theoretical studies have shown scanning curves can cross if the pore structure contains a mixture of pores that fill/empty as independent pores and pores that fill/empty through cooperative pore effects (advanced adsorption and pore blocking) [5]. Therefore, it is not possible to simply conclude that a porous system is made up of independent pores if gas sorption scanning curves ‘cross’. Hence, given this ambiguity in interpretation, more work is required to improve the understanding of the origins of the various forms of scanning curves.

While detailed studies [6,7] of gas sorption in model, ordered porous solids, such as MCM-41 and SBA-15, have improved understanding of gas sorption in relatively simple void space geometries, extending these results to disordered, amorphous materials, such as sol–gel silicas, is not straightforward. The improved accuracy in pore size determination using non-local density functional theory (NLDFT) relies upon the relevance of uniform pore geometry to a disordered solid, and an assumed knowledge of the pore-filling and emptying mechanisms, such as whether they are spinodal, equilibrium, or other, processes. However, NMR cryodiffusometry studies [8,9] have shown that the pore-filling mechanism varies along the adsorption branch for disordered solids. The algorithms used for deconvolving PSDs from gas sorption isotherms also do not include co-operative adsorption effects, such as advanced adsorption, that studies have shown are clearly present in adsorption data for disordered solids [8,9]. This is because the boundary adsorption curve is insufficient, on its own, to detect these effects, and additional information is required. In this work, the extent to which sorption scanning experiments can provide complementary information will be assessed.

The aim of this work is to utilise gas sorption scanning curve experiments, in series, before and after a mercury porosimetry experiment (the integrated gas sorption–mercury porosimetry–gas sorption experiment [10]), in order to assess how well previous theories of scanning curves can account for the observations. In particular, the concept that an interconnected network of pores can be described as a set of ‘independent’ pores if scanning curves cross directly between the boundary curves will be tested. To the best of our knowledge, there has been no experimental test to determine which particular mechanism is occurring when scanning curves cross between the boundary curves. The integrated gas sorption (scanning curve)–mercury porosimetry–gas sorption (scanning curve) experiment, potentially, represents an appropriate experimental test to establish the cause of crossing scanning curves. This is because gas sorption data for the pores which entrap mercury can be deconvolved from that for all other pores, and the scanning curves for these pores can then be determined. It is also an aim of this work to show that the additional sensitivity obtained via the integrated gas sorption and mercury porosimetry experiment is necessary, when studying disordered mesoporous materials, in order to obtain accurate PSDs.

## 2. Theory

### 2.1. Gas sorption scanning curves

Crossing scanning curves are generally thought to occur when open cylindrical pores fill and empty independently. This was originally predicted by independent domain theory [3]. To explain this in detail, a structural simple model will be used (Fig. 1) and the corresponding gas sorption schematic, for the pore model, is presented in Fig. 2. The pore model is made up of three domains, p1, p2 and p3, where the diameter of  $p_3 > p_2 > p_1$  and the volume of each domain is the same. The domains, although connected, do not interact with one another, so each domain will fill and empty independently. Furthermore, the domains will fill in order of increasing size, empty in order of decreasing size and the adsorption pressure is greater than the desorption pressure. The corresponding gas sorption schematic (Fig. 2) is now explained. The abscissa is the relative pressure,  $P/P_0$ , and the ordinate is the amount adsorbed,  $n^a$ . As the pressure is increased, p1 becomes filled with condensate, which is indicated by stage A. As the pressure is increased further, p2 (stage B), and then p3 (stage C), become filled with condensate. On lowering the pressure, p3 empties (stage E), and, on lowering the pressure further, p2 empties (stage F). The point where the pore model is completely empty of condensate has not been shown, in Fig. 2, to improve the clarity of the schematic. In addition, desorption scanning curves can be achieved by reversing the direction of pressure change at stages A and B on the adsorption curve. Alternatively, adsorption scanning curves can be achieved by reversing the direction of pressure change at stages E and F on the desorption curve. The desorption scanning curve from stage B to E will now be described in detail. At stage B on the adsorption curve domains p1 and p2 are filled. On reversing the direction of pressure change, to start the desorption scanning curve, domain p2 will not empty until at least stage E has been reached. The desorption scanning curve will therefore cross directly from the adsorption boundary curve to the desorption curve between stages B and E. An analogous explanation can be used to explain that the adsorption scanning curves will cross from stages E and F to stages B and A respectively.

Desorption scanning curves can also cross when both advanced adsorption and pore blocking effects occur. This is now explained using the pore structural model shown in Fig. 3, and its corresponding gas sorption schematic (Fig. 4). The pore model (Fig. 3) is made up of four domains, where the diameters are such that  $p_4 > p_3 > p_2 > p_1$ . In this pore model it is assumed that domains can interact, and they do so in the following way. Once p1 becomes filled with condensate, the size of the neighbouring domain, p2, is considered to be such that a hemispherical meniscus can then ingress into it, via the advanced adsorption mechanism. Due to the relatively larger size differences of nearest neighbours, the domains p3 and p4 will fill independently, and, thus, are not filled by an advanced adsorption mechanism. Upon desorption, due to pore-blocking effects, p4 can empty only if p3 is empty of condensate, and p2 can empty only if p1 is empty of condensate. In addition, the void volume of each domain is the same. The

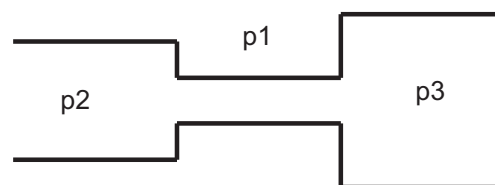


Fig. 1. Pore structural model made up of domains. The diameter of each domain is such that  $p_3 > p_2 > p_1$ .

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