

# Detection of the delayed condensation effect and determination of its impact on the accuracy of gas adsorption pore size distributions



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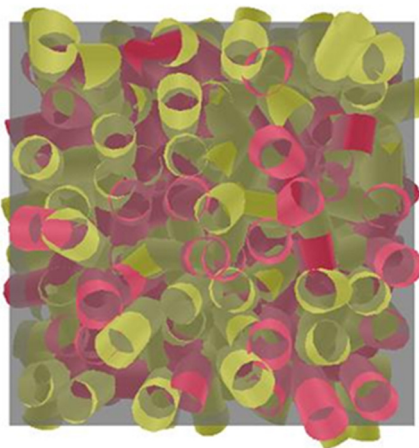
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## HIGHLIGHTS

- Novel pore structure characterisation technique utilizing two adsorptives.
- More accurate pore size measurement for disordered materials.
- Determine particular reason for delayed adsorption in given material.
- Understand cause of sorption hysteresis width in complex void spaces.

## GRAPHICAL ABSTRACT

Characterising disordered pore networks.



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## ABSTRACT

Macroscopic, highly disordered, mesoporous materials present a continuing challenge for accurate pore structure characterization. The typical macroscopic variation in local average pore space descriptors means that methods capable of delivering statistically representative characterizations are required. Gas adsorption is a representative but indirect method, normally requiring assumptions about the correct model for data analysis. In this work we present a novel method to both expand the range, and obtain greater accuracy, for the information obtained from the main boundary adsorption isotherms by using a combination of data obtained for two adsorptives, namely nitrogen and argon, both before and after mercury porosimetry. The method makes use of the fact that nitrogen and argon apparently 'see' a different pore geometry following mercury entrapment, with argon, relatively, 'ignoring' new metal surfaces produced by mercury porosimetry. The new method permits the study of network and pore-pore co-operative effects during adsorption that substantially affect the accuracy of the characteristic parameters, such as modal pore size, obtained for disordered materials. These effects have been explicitly quantified, for a typical sol-gel silica catalyst support material as a case study. The technique allowed the large discrepancies between modal pore sizes obtained from standard gas adsorption and mercury thermoporometry methods to be attributed to the network-based delayed condensation effect, rather than spinodal adsorption.

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Once the network-based delayed condensation effect had been accounted for, the simple cylindrical pore model and macroscopic thermodynamic Kelvin-Cohan equation were then found sufficient to accurately describe adsorption in the material studied, rather than needing a more complex microscopic theory. Hence, for disordered mesoporous solids, a proper account of inter-pore interactions is more important than that of intra-pore adsorbate density distribution, to obtain accurate pore size distributions.

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## 1. Introduction

Gas adsorption is still an extremely common method used to obtain pore size distributions (PSD) for disordered porous solids. The typical PSD obtained is a probability density function for pore size weighted by volume. A similar descriptor can be obtained using mercury porosimetry. This descriptor is used to understand the performance of such materials as heterogeneous catalyst pellets, adsorbents, chromatographic media, and many other applications. While the gas adsorption and mercury porosimetry methods are indirect, unique pore size distributions can be obtained for some materials using particular techniques for the simultaneous inversion of mercury intrusion and nitrogen sorption curves [1].

In addition, many recent workers [2,3] have attempted to use a range of tomographic methods to more directly study the void space. Methods such as electron tomography and dual beam scanning electron microscopy can obtain nanometre-resolution images of the void space, and thus image the nanoporous materials that can also be probed by gas adsorption. However, the imaging methods can only obtain images for samples of sizes of  $\sim 500$  nm at nanometre resolution, and, thus, it must be assumed that the volume sampled is representative of the pellet as a whole. While it is sometimes found that the characteristic size, of the particular volume of sample imaged, exceeds the correlation length of the local void space, combined mercury porosimetry and computerised X-ray tomography (CXT) studies [4] have also shown that many disordered materials are macroscopically heterogeneous, as well as microscopically heterogeneous. Combined CXT and mercury porosimetry allowed the macroscopic length-scale spatial variation in the penetration of nanopores by mercury up to a particular pressure to be monitored. The pore structures of many disordered materials may be such that local regions with statistically-similar properties may only exist over length-scales up to  $\sim 100$   $\mu\text{m}$ , at the most, but other similarly-sized regions may exist elsewhere within the pellet with very different characteristic properties. This means that it is, in principle, necessary to image the whole macroscopic pellet (typically of length-scales  $> \text{mm}$ ) to obtain information representative of the whole network of (typically)  $\sim 10^{14}$  pores within the pellet. However, this is currently physically impossible with current imaging and computer technology limitations. In contrast, gas adsorption can deliver statistically-representative information for a whole pellet, or even a small bed of pellets. Further, PSDs are also often much quicker and cheaper to obtain by gas adsorption, than by imaging, and thus are still popular in industry. There is thus still a need for accurate gas adsorption data.

However, research on the fundamental physical processes involved in gas adsorption in complex pore geometries has revealed the existence of certain effects that reduce the accuracy of PSDs thus obtained. These effects are known as advanced [5] and delayed [6] filling (or condensation, or adsorption). These particular effects are pore-pore co-operative in nature, and thus the size of the effects is associated with the random inter-connectivity of pores of various different sizes within disordered solids, and, thence,

studies of the more regular structures possessed by templated materials does not help to elucidate the actual extent of these problems in a given disordered material. The basic underlying principle of advanced condensation can be best understood in the context of a model through 'ink-bottle' pore. If the pressure for condensation, via a cylindrical sleeve meniscus, in the empty necks of the ink-bottle exceeds the pressure for condensation, via a hemispherical meniscus in the body, then all pore segments will fill at once because condensation in the necks creates hemispherical menisci at the ends of the body. Delayed condensation occurs when the pore potential in a given pore is reduced, below that for a void of the same geometry but with completely solid walls, due to side-arms branching off that pore leaving gaps in the walls.

The potential impact of the co-operative phenomena on PSD accuracy has been demonstrated by computer simulation of adsorption in pore network models [7]. Matadamas et al. [7] have simulated the effects of delayed and advanced adsorption in pore body-pore neck network models with a range of pore connectivities, and overlaps between pore body and neck size distributions. They compared the actual pore space characteristics of the underlying models with those obtained, by standard analysis methods, from the simulated isotherms, and showed that delayed condensation gave rise to a significant error in the accuracy of the PSD derived.

Attempts have been made to study pore-pore co-operative effects with gas sorption scanning curves but the data from these experiments are a composite signal from the whole sample, and thus difficult to interpret unambiguously for disordered solids, as opposed to more ordered templated solids [6]. In contrast, the novel integrated gas sorption and mercury porosimetry technique, which involves conducting a series of gas sorption and mercury porosimetry experiments on the same sample, can study pore-pore co-operative effects in particular sub-sets of pores within disordered samples by deconvolving-out the signal from these pores. Previous work with this technique has demonstrated the existence of advanced adsorption of nitrogen in disordered silica gel materials [5], but has not studied delayed condensation. More recently the integrated gas sorption and mercury porosimetry technique has shown that there is a difference in the wetting of solid mercury relative to silica for nitrogen and argon adsorbates at their boiling points [8]. It was found that nitrogen will readily wet solid mercury surfaces, while argon, relatively, does not very much. As will be described in more detail below, in this work, this newly found effect will be used to demonstrate the presence of delayed condensation in gas adsorption in a typical catalyst support pellet as a case study. The mercury porosimetry data also available from the integrated experiment allows alternative interpretations of the gas sorption data to be discounted, and a definitive interpretation to be obtained. In order to determine the impact of the delayed condensation on PSD accuracy the pore sizes will also be measured independently using mercury thermoporometry, and also  $^1\text{H}$  NMR cryoporometry.

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