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Experimental and modelling studies of the kinetics of mercury retraction from highly confined geometries during porosimetry in the transport and the quasi-equilibrium regimes

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ABSTRACT

Mercury porosimetry is a widely used method for pore structural characterisation but, often, half of the data obtained in any given experiment, in the form of the retraction curve, is simply not used. This may be because mercury retraction is significantly less well understood than intrusion, and thus it is more difficult to extract reliable information. In this work, detailed studies have been made of the retraction process from mesoporous materials, with non-random heterogeneities in their void structure, to obtain fundamental knowledge that could form the basis of methods to reliably extract accurate pore space descriptors from the retraction curve. In one material the initiation of retraction was found to be independent of the experimental time-scale because it was governed by the rapid equilibration of the narrowing of mercury necks, and subsequent snap-off of mercury connections at a small number of pore intersections. This scenario has been validated by simulations of quasi-equilibrium mercury retraction on structural models obtained from magnetic resonance images. In another material, the slow relaxation of entrapped mercury was followed by integrated gas sorption experiments and SAXS. This process was also simulated using Monte-Carlo methods. It was found that the temporal evolution of the remaining pore size distribution was sensitive to the initial configuration of entrapped mercury ganglia, and could thus be used to validate specific models of mercury entrapment for particular amorphous materials.

1. Introduction

Mercury porosimetry is a widely used pore characterisation method, particularly in the catalyst and oil industries. Its main advantage over other methods is that it is possible to probe pore sizes over the vast range of length-scales from ~100 μm to ~3 nm with the same technique. This is of particular importance for materials, such as cement (Moro and Böhni, 2002) or carbonate rocks (Wardlaw et al., 1988), that possess pores of sizes over several orders of magnitude. Unlike many tomography techniques, such as 3D-transmission electron microscopy (3D-TEM) (Koster et al., 2000), dual beam microscopy (Holzer et al., 2004), or X-ray tomography (Ruffino et al., 2005), mercury porosimetry, particularly in combination with complementary structural characterisation methods, such as magnetic resonance imaging (MRI) (Rigby, 2000), is able to obtain detailed, statistically representative information on the whole void space for macroscopically (> 10 μm) heterogeneous, nanoporous materials. Mercury porosimetry is based on the principle that mercury is a non-wetting fluid for most solids and thus an external pressure must be imposed to force the liquid into the pores. This pressure is generally given by the version of the Young–Laplace equation commonly referred to as the Washburn (1921) equation, where pressure is inversely related to pore size. Hence, the mercury will enter large pores, at first, as the pressure rises, followed by smaller pores.

The simplest derivation of the Washburn equation generally only involves a consideration of the mechanical equilibrium of the pressure and capillary forces within a pore. However, as described by Kadlec (1985), for smaller pores, the dispersion forces between mercury and the solid phase, and the change in chemical potential of mercury corresponding to the change of its structure in the force field in pores just being filled, must also be considered. Since, as described above, mercury porosimetry is often used to characterise materials with a wide pore size range, including those down to nanometer dimensions, it is important to understand the effects of

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extreme geometric confinement of mercury on the interpretation of raw porosimetry data. These effects manifest themselves in changes to the surface tension and contact angle for mercury with pore size, and in other ways discussed below.

The most commonly used experiment in porosimetry consists of increasing the pressure in small steps and measuring the resultant volume of mercury entering the sample, after allowing the system to reach equilibrium following a pressure step. If it is assumed that the porous material has a void space structure analogous to a parallel bundle of pores then the mercury intrusion curve can be converted directly to a volume-weighted pore diameter distribution using the Washburn equation. However, most materials have a more complex void space structure than this, and thus the pore 'shielding', or 'shadowing', effect may arise. This effect occurs because larger pores may only have access to the material surface just by routes via smaller-sized pores. Hence, the pressure must rise sufficiently for mercury to enter these shielding pores before entering the shielded, larger-sized pore. Many different structural models for interpreting mercury porosimetry data have been suggested to take this effect into account, and thereby render a more accurate, 'deshielded' pore size distribution. These models are generally based on random pore networks (Fatt, 1956; Androutsopoulos and Mann, 1979).

In general, much less use is made of the mercury retraction curve, also obtained as part of the standard experiment, when the pressure is reduced back to ambient in small steps. The retraction curve is generally associated with hysteresis and entrapment. The mercury generally leaves the sample at a lower pressure than was required to force it into the structure initially, and some mercury is often (apparently) permanently retained within the pores when the pressure has been returned to ambient. However, the retraction curve is also potentially a source of useful information concerning the pore structure. In porosimetry simulation work, the retraction curve has been used to validate pore-bond network structural models obtained using the intrusion curve (Mann and Golshan, 1981; Mata et al., 2001), test models for the pore-scale mechanisms of meniscus retraction and snap-off (Tsakiroglou et al., 1997; Tsakiroglou and Payatakes, 1998), and obtain information about pore connectivity (Portsmouth and Gladden, 1991, 1992), or the spatial arrangement of pore sizes (Rigby, 2000). However, if the method to obtain pore space descriptors from mercury retraction is based on an inaccurate model of the underlying physical process, then the pore space descriptors thereby obtained will have little validity.

Androutsopoulos and Mann (1979) proposed that the retraction of mercury may involve a (slower) relaxation process, as well as the, presumably much more rapid, capillary flow of mercury described by Washburn (1921) and Wardlaw and McKellar (1981). The slow retraction process is attributed to the formation of isolated 'packages', or ganglia, of entrapped mercury that, under the action of a non-zero net force prior to equilibration, tend to move around slowly and occasionally coalesce with the bulk. Hence, interpretation of the mercury retraction curve solely in terms of piston-like retraction may be incorrect. In earlier work, as the relaxation process was presumed slow, it was neglected in interpreting mercury retraction curves and in simulations of porosimetry (Androutsopoulos and Mann, 1979).

Much of the simulation of porosimetry work carried out previously has used network models for void space structure, and percolation processes to model the pore-scale mercury displacement. However, recently molecular dynamics (Martic et al., 2002), lattice-Boltzmann (Hyvaluoma et al., 2007), and statistical mechanics (Porcheron et al., 2007) methods have been used to simulate porosimetry on structural models obtained directly from full 3D X-ray tomographic reconstructions of void spaces (Hyvaluoma et al., 2007), or statistical reconstructions based on scattering data (Porcheron et al., 2007). The main drawback with these simulation techniques is that only a potentially unrepresentative microscopic fraction of the void space of a potentially macroscopically heterogeneous mesoporous solid can be represented on computer. However, the lattice-Boltzmann simulations conducted in the X-ray tomographic reconstructions (Hyvaluoma et al., 2007) validated the invasion percolation model for mercury intrusion into disordered materials. In addition, the statistical mechanical modelling of porosimetry suggests that mercury retraction involves two different dynamical regimes. The first regime, known as the transport regime, is associated with mass transfer to the external surface, while the second regime, known as the quasi-equilibrium regime, corresponds to re-distribution of the fluid inside the material. In general, the experimental time-scale exceeds the typical time-scale of the transport regime but not necessarily the quasi-equilibrium regime. In the statistical mechanical simulations, the mass transport even in the transport regime was considered to be diffusional relaxation. Most other workers in mercury porosimetry have considered mass transport to occur by viscous flow processes (Wardlaw and McKellar, 1981; Tsakiroglou et al., 1997; Tsakiroglou and Payatakes, 1998). However, there has been little, or no, experimental studies of the actual rates of the quasi-equilibrium, or relaxation, process involved in mercury retraction.

A comparison of the shapes of mercury retraction curves simulated using statistical mechanics (Porcheron et al., 2007) with experimental data suggests that the simulations do not accurately re-create the shape of the initial knee in the high pressure region of the experimental retraction curves. In the new work presented here, mercury porosimetry experiments were conducted with varying experimental time-scales in order to study the transport regime in detail, and, in particular, the initiation of mercury retraction not well captured by statistical mechanical models. Materials were also examined over even longer time-scales after the initial porosimetry experiment to study the quasi-equilibrium regime. Monte-Carlo simulations of the quasi-equilibrium regime have been compared with experimental data from integrated gas sorption experiments and SAXS. There is very little previous work employing scattering methods to study mercury porosimetry (Makri et al., 2000). These data will be used to infer the initial spatial arrangement of entrapped mercury for amorphous, nanoporous materials, and thereby aid the understanding of the retraction process and entrapment mechanism.

The detailed study of mercury retraction is important for interpreting data from integrated gas sorption experiments for studying the fundamentals of adsorption processes (Rigby et al., 2008), or to obtain a wider range of pore space descriptors, such as pore length (Rigby et al., 2004). Integrated gas sorption and mercury porosimetry experiments consist of a series of gas sorption and porosimetry runs conducted in series on the same sample, with any entrapped mercury frozen in-place at 77 K before conducting the next gas sorption experiment. Much of the data analysis of integrated gas sorption experiments relies on entrapped mercury remaining within the particular pores suggested by the previous mercury retraction curve. Hence, it is important to understand any mercury mass transport processes that may occur before the mercury is frozen in-situ. In addition, as stated above, the mercury retraction curve potentially contains valuable information about the nature of the void space structure, that a better understanding of the retraction process will enable to be realised. It will be shown here that a study of the relaxation of entrapped mercury following porosimetry enables the likely original mechanism of mercury entrapment to be determined. Once the mechanisms of mercury retraction and entrapment have been identified interpretation of the retraction curve would become more reliable. The migration of non-wetting fluids within porous media is also of more general interest in areas such as soil remediation and enhanced oil recovery (Meakin et al., 2000).

In order to study the effects of extreme geometric confinement on mercury behaviour and better understand the mercury retraction