Uncertainty in pore size distribution derived from adsorption isotherms: II. Adsorption integral approach

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ABSTRACT

Uncertainty in the amount adsorbed in manometric adsorption isotherm measurements is well established. Here, we extend uncertainty methodologies from adsorption isotherm data uncertainty and apply them to calculate pore size distributions based on adsorption integral methods. The analyses consider as variables: uncertainty in adsorption isotherm data, regularization parameter, molecular potential model, and the number of single pore isotherms calculated with an associated quadrature interval. We demonstrate how the calculated pore size distribution is quite insensitive to the uncertainty in experimental data, but in contrast, the uncertainty in the experimental data affects the calculated value of the optimized regularization parameter which, in turn, leads to considerable variation in the calculated pore size distribution. The calculated pore size distribution is also shown to be highly dependent on the potential model selected and on the number of single pore isotherms applied to the inversion process. We conclude and suggest a quantitative comparison between calculated pore size distributions should be discouraged unless the uncertainty in the experimental data is relatively small and, default values for regularization parameters, potential models, the number of single pore isotherms and their distribution are exactly the same for each pore size distribution evaluation.

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1. Introduction

Gas adsorption measurement has been applied to a diverse range of powders and porous materials for surface characterization in terms of surface chemistry and surface density of bound functional groups, and for the determination of physical properties including: specific surface area; pore connectivity, and pore size distribution (PSD) [1]. Over the past 2-3 decades, elaborate computer programs for molecular modelling have resulted in significant advances in porous materials characterization, particularly for PSD determination.

Porous materials offer challenging experimental and theoretical demands for an unequivocal interpretation of the PSD. In most cases, the anticipated complex internal structure, due to interconnected, irregularly-shaped pores of different sizes are simplified by assuming a distribution of equivalent, regularly-shaped, entities such as slit or cylinder pores. Porous materials derived from naturally-sourced materials usually offer more complex internal structures than those developed synthetically via a well-established recipe. In addition to this, pore connectivity is not considered in PSD determination models, effect of functional groups and their distribution on the surface is ignored and interaction between neighbouring pores is neglected. Hence, calculated PSD must be regarded as "effective pore size distribution" [2]. Despite the above shortcomings and simplifying assumptions, adsorption based PSD determination methods are still considered powerful tools for PSD determination. These methods can be classified into two main categories: classical methods and the integral equation approach.

Due to differences in pore filling and fluid—solid interaction mechanisms, the classical thermodynamics-based methods for PSD determination developed separately for micropores and mesopores [3]. The more recent methods for PSD determination are based on

an inversion of the adsorption integral equation; for a single component adsorptive it can be written as:

$$N(T,P) = \int_0^\infty \rho(w,T,P)f(w)dw \qquad (1)$$

Here, $N(T,P)$ is the experimental adsorption isotherm data at a given temperature T and pressure P. The function $\rho(w,T,P)$ represents a series of simulated isotherms nominally as single pore isotherms or SPIs (kernels) for the same adsorptive within an ideal-shaped pore of a specified dimension, w, and $f(w)$ is a pore size distribution function. The integration limits as cited are typically adjusted to accommodate the minimum and maximum pore sizes to be defined via the simulated SPIs. A PSD derived from the adsorption integral equation method is classified via the approach taken to calculate the SPI. These isotherms can be developed via either molecular dynamics (MD) calculations, a Monte Carlo (MC) simulation, or using a Density Functional Theory approach. The inversion of the adsorption integral equation is independent of the SPI-generation method.

The MD method solves Newton's equations of motion to calculate velocities and positions of a set of particles that are adsorbed by a simulated porous solid [1]. In MC simulation, SPIs are calculated by using a Grand Canonical ensemble (GCMC) as a μVT ensemble [4]. This method usually has shorter processing times compared to the MD method. The density functional theory correlates the whole system energy (Grand Potential Energy or GPE) as a function of particle density distribution within the system. The particular density distribution of particles that minimizes the GPE is considered to be the equilibrium density distribution [2]. DFT calculations require considerably less computational time than MD or MC methods, and yields equivalent equilibrium predictions. Wu presented a review of DFT applied to various molecular simulations [5].

Evans et al. introduced DFT to model gas adsorption as capillary condensation in well-defined pores [6,7], with the method subsequently extended by Seaton et al. using a local DFT to define the PSD in a porous activated carbon [8]. Lastoskie et al. [9] modified this approach using a non-local DFT (NLDFT) model proposed by Tarazona et al. [10] for PSD calculation. A comparison of these methods indicates the provision for short-ranged correlations in the fluid density within the NLDFT yields a superior estimation of adsorbed phase density. This method has been widely used for PSD determination in the literature and is now adopted as a standard for PSD analysis by the International Standard Organization (ISO) [11].

The NLDFT and previous molecular modelling methods assumed homogeneous, structurally smooth pore walls at the atomic scale. As a consequence of this simplifying assumption, NLDFT-modelled SPIs exhibit steps corresponding to molecular layering effects, eventually resulting in the appearance of artificial gaps in the calculated PSD. Neimark and co-workers later proposed the Quenched Solid Density Functional Theory (QSDFT) for silica-based [12] and carbon-based [13] materials by accounting for surface heterogeneity and roughness effects as a distribution of solid atoms on the surface and via the introduction of a single roughness parameter. The resulting SPIs for nitrogen and argon resulted in "smoother" isotherms with no layering steps, and a superior fit to the experimental data [14]. Landers et al. provide a review of recent advances in DFT methods for porous material characterization [15].

An application advantage of the adsorption integral equation method over the classical thermodynamics-based methods for PSD analysis derives from the uninterrupted range of pore sizes, from the smallest micropore to the largest mesopore, based on a gas adsorption isotherm from the lowest measureable relative pressure up to saturation. A disadvantage is due to the limited number of SPI libraries available in the literature confined to a few adsorptives at specific temperatures. Nonetheless, since the integral methods accommodate the entire (nitrogen-based) pore size distribution(s) and pedagogically are based on fewer initial assumptions compared to classical methods, the adsorption community is accepting them as standard characterization methods.

For gas adsorption analysis of adsorbents, we suggest that at least two distinct categories of uncertainties need to be recognized. Experimental data uncertainty is the variation of the actual measured parameter leading to a combined uncertainty in the experimental result. Only a few studies of adsorption uncertainty are available in the literature. Loebenstein and Deitz introduced large dead-spaces in sampling tubes as the main sources of uncertainty in adsorption data [16]. Ross and Olivier addressed uncertainty corresponding to apparatus calibration [17]. Robens et al. investigated the non-ideal behaviour contributions of helium and nitrogen [18]. The effect of liquid nitrogen level control on adsorption results was first reported by Killip et al. [19]. Badalyan and Pendleton built an automated manometric gas adsorption apparatus, calibrated dosing and sample volumes and propagated uncertainty for each adsorption isotherm result [20,21]. They introduced sample mass measurement, liquid nitrogen-level control, and dead-volume determination as the main sources of uncertainty in experimental data. Secondly, further analysis derived from the isotherm data, such as BET specific surface area, α_S-analyses, and pore volume showed an increase in their respective values [22,23]; PSD analysis would also introduce additional combined uncertainty. Recently Caguiat et al. suggested an interpretation of PSD in nanoporous adsorbents. They suggested that a proper interpretation of the PSD relies on the correct selection of SPIs and adsorptives [24]. Their study examined four different carbon porous materials and their PSDs were calculated by using commercial and DFT theory.

In contrast with uncertainty in PSD analyses due to the application of classical thermodynamics methods [25], the present work begins by identifying the optimum parameters for the inversion of the adsorption integral equation to define an optimized PSD. To make a parametric analysis, we consider holding all but one of the variables constant at the optimized value, then examine the effect of variation of the variable on the resulting PSD. In some cases, it was necessary to adjust two of the variables to fully appreciate the impact of change on the resulting PSD. The variables considered were the combined standard uncertainty in the amount adsorbed, the value of the regularization parameter, the molecular model employed to calculate the SPIs, and the influence of the number of SPIs on the PSD.

2. Methods

2.1. Experimental measurements

Single sheet, plain-weaved activated carbon cloth (ACC) FM1/250 (ex. Calgon Carbon, Pittsburgh, PA, USA) was used as it showed a narrow PSD in the micropore range [26]. Samples were degassed prior to the experiments at 200 °C and a background vacuum of 0.1 mPa for 8 h. Thermal transpiration effects were accounted for at pressures below 266 Pa. Throughout the adsorption−desorption process the liquid nitrogen level was controlled constant ±0.15 mm. Ultra-high purity (99.999%) helium and nitrogen (ex. BOC Gases, Adelaide, Australia) were used for dead-space measurements and adsorption experiments, respectively. The adsorption isotherm data were obtained using the adsorption apparatus presented in Refs. [20], and the uncertainty in the amount adsorbed propagated